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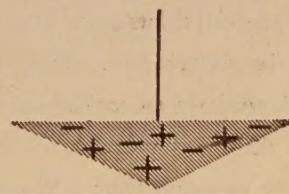
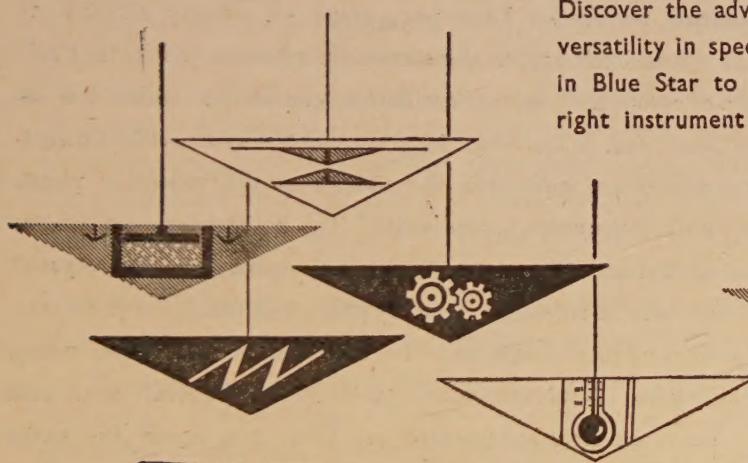
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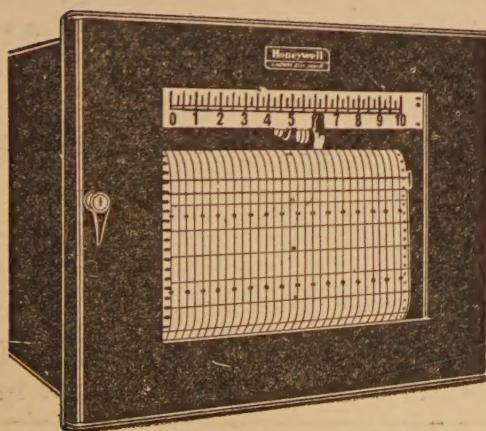
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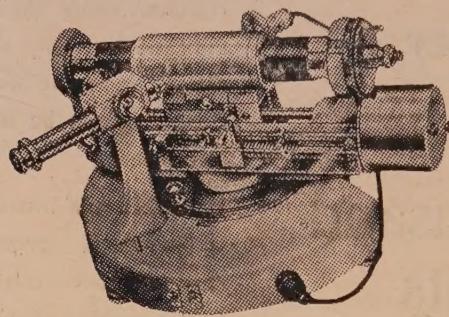
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A NOTE ON THE PROBLEM OF INTRODUCING SPHERICITY CORRECTION TO CONSERVATIVE SCATTERING STELLER ATMOSPHERE MODEL

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(Received, March 21, 1960)

ABSTRACT. The relative magnitude of the correction to be applied for the curvature in the study of the radiative transfer problem in the conservative scattering stellar atmosphere has been calculated. Wick-Chandrasekhar method of solution for the integro-differential equation of transfer has been employed in the first approximation. The results are shown in a tabular as well as graphical form.

The problem of transfer of radiation in the case of extended atmospheres of stars in which the curvatures of the layers of atmospheres has significant effect on the transfer problem, has been considered by Kosirev (1934) and Chandrasekhar (1934). On the other hand, it is quite well known in the theory of radiative transfer that for most stars such as the sun, the atmosphere can be considered to be plane parallel. In a recent paper, Barbier (1956) discussed the problem for near solar case and established that it is not necessary to consider the atmosphere as spherically symmetrical. The purpose of the present note is to examine the magnitude of correction involved in passing from plane parallel to the spherically symmetrical case for different values of optical thickness of the stellar atmosphere in the conservative scattering case.

In the present case, the atmosphere chosen is thin, finite and conservative scattering. The equation of transfer appropriate to the problem of spherically symmetric atmosphere is given by (Radiative Transfer—Chandrasekhar, p. 364)

$$\mu \frac{\partial I(r, \mu)}{\partial r} + \frac{p - \mu^2}{r} \frac{\partial I(r, \mu)}{\partial \mu} = -k\rho I(r, \mu) + \frac{1}{2}k\rho \int_{-1}^{+1} I(r, \mu') d\mu' \quad \dots \quad (1)$$

and appropriate equation for the plane case is given by

$$\mu \frac{dI}{dr}(r, \mu) = -k\rho I(r, \mu) + \frac{1}{2}k\rho \int_{-1}^{+1} I(r, \mu') d\mu' \quad \dots \quad (2)$$

Here $I(r, \mu)$ is the specific intensity of radiation at a distance r from the centre of the star in a direction μ where $\mu = \cos \nu$, ν being the angle between the direction of the ray and the outward drawn normal to the atmosphere. Both of

these equations are solved by the method of Wick-Chandrasekhar in the first approximation. Thus Eq. (1) is transformed into the following group of equations (Radiative Transfer—Chandrasekhar, p. 366) :

$$\left. \begin{aligned} \frac{d}{dr} \Sigma a_i \mu_i I_i + \frac{2}{r} \Sigma a_i \mu_i I_i &= 0 \\ \frac{d}{dr} \Sigma a_i \mu_i^2 I_i + \frac{1}{r} \Sigma a_i (3\mu_i^2 - 1) I_i &= -k\rho \Sigma a_i \mu_i I_i \end{aligned} \right\} \dots (3)$$

And for the plane parallel case, the Eq. (2) can be written out formally by dropping out the second term on the right hand side of (1) and that in the Eq. (129) of Radiative Transfer, p. 366.

$$\left. \begin{aligned} \frac{d}{dr} \Sigma a_i \mu_i I_i &= 0 \\ \frac{d}{dr} \Sigma a_i \mu_i^2 I_i &= -k\rho \Sigma a_i \mu_i I_i \end{aligned} \right\} \dots (4)$$

In the case of the first approximation $a_{+1} = a_{-1} = 1$ and $\mu_{+1} = \frac{1}{\sqrt{3}} = -\mu_{-1}$.

The boundary conditions under which the equation is to be solved are the following :

- (1) At the inner boundary of the atmosphere denoted by $r = r_0$, the outward intensity I_{+1} is very strong in comparison with I_{-1} , the inward intensity.
- (2) At the outer boundary of the atmosphere denoted by $r = R$, there is no incident radiation from outside (I_{-1} is zero).

The solution of the first of Eqs. (3) yields

$$\frac{1}{2} F = \Sigma a_i \mu_i I_i = \frac{1}{2} \cdot \frac{F_0}{r^2}, \text{ where } F_0 \text{ is a constant.}$$

Hence

$$I_{+1} - I_{-1} = \frac{\sqrt{3}}{2} \cdot \frac{F_0}{r^2} \dots (5)$$

The second of Eq. (3) solves as

$$\frac{1}{3} \frac{d}{dr} (I_{+1} + I_{-1}) = -\frac{k\rho}{\sqrt{3}} (I_{+1} - I_{-1}) = -\frac{k\rho}{2} \cdot \frac{F_0}{r^2}$$

$$(I_{+1} + I_{-1}) = \frac{3}{2} F_0 \int_r^R \frac{k\rho dr}{r^2} + A \dots (6)$$

where A is a constant, and this can be determined by the boundary condition (1)

$$A = \frac{\sqrt{3}}{2} \cdot \frac{F_0}{r_0^2} - \frac{3}{2} F_0 \int_{r_0}^R \frac{k\rho dr}{r^2} \quad \dots \quad (7)$$

$$\therefore I_{+1} + I_{-1} = \frac{\sqrt{3}}{2} \cdot \frac{F_0}{r_0^2} - \frac{3}{2} F_0 \int_{r_0}^R \frac{k\rho dr}{r^2} + \frac{3}{2} F_0 \int_r^R \frac{k\rho dr}{r^2} \quad \dots \quad (8)$$

At $r = R$, the outer boundary of the atmosphere

$$(I_{+1})_{r=R} = \frac{\sqrt{3}}{2} \frac{F_0}{r_0^2} - \frac{3}{2} F_0 \int_{r_0}^R \frac{k\rho}{r^2} dr \quad \dots \quad (9)$$

In the plane case, we can proceed in the similar way. The solution of the first of the Eq. (4)

$$\sum a_i \mu_i I_i = \frac{1}{2} F = \frac{1}{2} \frac{F_0}{r_0^2} \quad \dots \quad (10)$$

where F_0 and r_0 have the same meaning as before. The flux is constant in the plane parallel case

$$\therefore I_{+1} - I_{-1} = \frac{\sqrt{3}}{2} \frac{F_0}{r_0^2} \quad \dots \quad (11)$$

The second of Eqs. (4) yields

$$I_{+1} + I_{-1} = \frac{3}{2} \frac{F_0}{r_0^2} \int_r^R k\rho dr + B \quad \dots \quad (12)$$

Using the boundary condition (1)

$$B = \frac{\sqrt{3}}{2} \frac{F_0}{r_0^2} - \frac{3}{2} \frac{F_0}{r_0^2} \int_{r_0}^R k\rho dr \quad \dots \quad (13)$$

$$\therefore I_{+1} + I_{-1} = \frac{\sqrt{3}}{2} \frac{F_0}{r_0^2} - \frac{3}{2} \frac{F_0}{r_0^2} \int_{r_0}^R k\rho dr + \frac{3}{2} \int_r^R k\rho dr \quad \dots \quad (14)$$

Then from the boundary condition (2), the incident radiation from outside at the outer boundary of the atmosphere may be taken to be zero

$$(I_{+1})_{r=R} = \frac{\sqrt{3}}{2} \frac{F_0}{r_0^2} - \frac{3}{2} \frac{F_0}{r_0^2} \int_{r_0}^R k\rho dr \quad \dots \quad (15)$$

In the astrophysical context, $k\rho$ is generally taken to vary as an inverse power of r (greater than unity)

$$\therefore k\rho = Cr^{-n}, \text{ where } C \text{ is a constant} \quad \dots \quad (16)$$

The optical thickness τ , measured from $r = R$ inwards is given by

$$\int_r^R k\rho dr = \frac{C}{n-1} \left[\frac{1}{r^{n-1}} - \frac{1}{R^{n-1}} \right] \quad \dots \quad (17)$$

$$\therefore \tau_1 = \frac{C}{n-1} \left[\frac{1}{r_0^{n-1}} - \frac{1}{R^{n-1}} \right] \quad \dots \quad (18)$$

i.e., $\tau = \tau_1$ denotes the photospheric surface at $r = r_0$. When $n = 2$, the emergent intensity $(I_{+1})_R$ for the spherical and the plane case is given by the two Eqns. (19) and (20).

For the spherical case

$$\frac{(I_{+1})_{\tau=0}}{\sqrt{\frac{3}{2}} F_0 / r_0^2} = (1 - \sqrt{3}\tau_1) + \frac{\tau_1}{\sqrt{3}} \left[2 - \frac{r_0}{R} - \frac{r_0^2}{R^2} \right] \quad \dots \quad (19)$$

and for the plane case

$$\frac{(I_{+1})_{\tau=0}}{\sqrt{\frac{3}{2}} F_0 / r_0^2} = (1 - \sqrt{3}\tau_1) \quad \dots \quad (20)$$

$$\therefore \frac{(I_{+1})_{\tau=0} \text{ (spherical)}}{(I_{+1})_{\tau=0} \text{ (plane)}} = 1 + \left[\frac{\tau_1}{\sqrt{3}(1 - \sqrt{3}\tau_1)} \left(2 - \frac{r_0}{R} - \frac{r_0^2}{R^2} \right) \right] \dots \quad (21)$$

The term within box bracket is obviously the term which arise from the curvature of the atmosphere and can be called sphericity correction in the present approximation for $n = 2$. The value of correction for different values of optical thickness τ_1 corresponding to several values $\frac{R-r_0}{r_0}$ are shown below in Table I.

The results are shown in Fig. 1.

In the similar way, it can be shown that for $n = 3$, the equation corresponding to (21) turns out to be

$$\frac{(I_{+1})_{\tau=0} \text{ (spherical)}}{(I_{+1})_{\tau=0} \text{ (plane)}} = 1 + \left[\frac{\sqrt{3}\tau_1}{2(1 - \sqrt{3}\tau_1)} \left(1 - \frac{r_0^2}{R^2} \right) \right] \quad \dots \quad (22)$$

The values of the correction terms within box bracket in the present approximation for $n = 3$ are noted below for different values of τ_1 and $\frac{R-r_0}{r_0}$ in Table II.

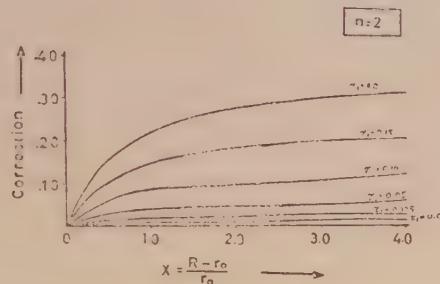


Fig. 1

TABLE I

$\tau_1 \backslash \frac{R-r_0}{r_0}$	0.25	0.50	1.00	2.00	4.00
0	0	0	0	0	0
0.01	0.003	0.003	0.007	0.009	0.010
0.025	0.008	0.013	0.019	0.023	0.026
0.050	0.018	0.028	0.037	0.047	0.056
0.10	0.039	0.062	0.087	0.098	0.123
0.15	0.066	0.104	0.146	0.182	0.206
0.20	0.099	0.157	0.221	0.275	0.311

TABLE II

$\tau_1 \backslash \frac{R-r_0}{r_0}$	0.25	0.50	1.00	2.00	4.00
0	0	0	0	0	0
0.01	0.003	0.004	0.006	0.008	0.008
0.025	0.008	0.011	0.017	0.020	0.021
0.05	0.017	0.025	0.033	0.040	0.046
0.10	0.038	0.055	0.078	0.084	0.101
0.15	0.064	0.093	0.131	0.156	0.168
0.20	0.095	0.140	0.199	0.236	0.254

The results are shown in Fig. 2.

From the graphs it is clear that there is no common region of applicability for the equation of transfer in the plane-parallel and the spherically symmetric

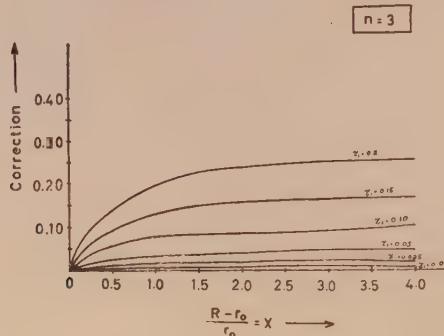


Fig. 2

case. As is physically expected, for any particular τ_1 , the smaller value of $\frac{R-r_0}{r_0}$, the smaller will be the magnitude of the correction term; and for any value of $\frac{R-r_0}{r_0}$, the smaller the value of τ_1 , the less significant will be the correction term.

In conclusion, the author takes pleasure in recording his gratitude to Prof. N. R. Sen for the benefit of discussion at the initial stage of the preparation of the paper and to Monsieur Spite of Laboratoire d'Astronomie, Lille, France for some active suggestions.

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THEORY OF INDIRECT EXCHANGE INTERACTION IN SPINEL-LIKE SYSTEMS*

K. P. SINHA

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(Received, September 1, 1960)

ABSTRACT. A theoretical study of the indirect exchange interaction for the spin coupling in spinel type magnetic compounds is made on the basis of a mechanism suggested by us recently. Detailed calculations are carried out for the elementary, four-centre ($A-O-B_2$; A and B represent the cations and O denotes the anion) and five-electron system. This furnishes the appropriate model for describing both $A-B$ and $B-B$ types of interactions.

The relative energies of the ferromagnetic (Quartet Q) and the two ferrimagnetic (Doublets D_1 and D_2) states are assessed for the above model. It is shown that, within the framework of the present mechanism, the ferrimagnetic state D_1 , which represents antiparallel spins in $A-B$ and parallel in $B-B$, is the most stable state. This is in agreement with the observed situation.

1. INTRODUCTION

Some recent papers (Anderson, 1959; Koide, Sinha and Tanabe, 1959) on superexchange interaction have led to a reappraisal of the types of mechanisms responsible for the spin coupling of magnetic ions in certain magnetic compounds (see also Kanamori, 1959; Keffer and Oguchi, 1959). It seems that of the various mechanisms proposed some are only apparently distinct and others embrace complementary features of the physical situation. However, it remains to establish as to which of these play the dominant role.

One of these mechanisms, which is analogous to spin-polarization around a nucleus that leads to nuclear indirect exchange was recently suggested by us (Koide, Sinha and Tanabe, 1959). It constitutes an important spin dependent effect and the contributions due to this mechanism needs to be fully assessed for each type of crystal structure while discussing the magnetic properties of such compounds. The previous paper, in addition to dealing with the general formulation of the mechanism in terms of semi-localized orbitals for the anion electrons, furnishes a quantitative calculation for the collinear three centre and four electron system applicable to magnetic compounds having rock salt or perovskite type structures. In another paper (Sinha and Koide, 1960), we have given a theoretical study of this interaction by choosing an elementary unit

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which is appropriate for zinc-blends type structures. In the present paper we give an analysis of the indirect exchange interactions in spinel-like systems, using, as in our previous papers, the Heitler-London method with the inclusion of the correlation effect which involves spin dependent transitions of the anion electrons.

2. THEORETICAL MODEL

It is appropriate to discuss briefly the relevant features of spinel structure before coming to the model chosen for calculation (for a fuller description of the structure see Gorter, 1954). The ideal spinel structure can be described as a cubic close packed lattice of anions (e.g., O^{2-}) with metal ions partly filling the tetrahedral (half of the 16 A sites) and the octahedral (half of the 32 B sites) interstices. There are eight molecules in the cubic unit cell, the molecular formula being AB_2O_4 . The immediate environment of each metal ion is thus cubic. The oxide ion, however, has four nearest neighbour metal ions of which three are at octahedral (B) sites and the fourth is in a tetrahedral (A) site. The three octahedral cations are situated at a distance R_0 along three mutually perpendicular directions from the oxide ion. The tetrahedral cation is in the $\langle 111 \rangle$ direction at a distance R_t and away from the octant which contains the three octahedral cations. The immediate symmetry around the oxide ion i.e., of the unit $A-O-B_3$ is described by the point group C_{3v} ; the next nearest neighbours of this oxide ion are twelve oxide ions of the face centred cubic lattice.

According to Neel's (1948) phenomenological theory for firrospinels, there are three types of negative interactions, namely A-A, B-B and A-B, the relative strengths of which determine the ultimate coupling; assuming, of course, the presence of one kind of magnetic ion (e.g., Fe^{3+}) only. If the AB interaction is much stronger than A-A and B-B interactions, the spin ordering $\vec{A} \overset{\leftarrow}{[B_2]}$ is favoured. This constitutes the fundamental assumption of the two sub-lattice model of Neel. However, when either of A-A and B-B interaction is comparable with A-B interaction, further generalizations as envisaged by Yafet and Kittel (1952) by dividing A into two sub-lattices A_1 and A_2 and B into four sub-lattices B_1 , B_2 , B_3 and B_4 , have to be considered. These considerations lead to certain triangular arrangements of the spin vectors associated with the sub-lattices.

The strengths of these interactions would depend on the nature and mechanism of the fundamental types of indirect exchange interactions involving the anion lattice as well as the cation-anion-cation angles and cation-cation and cation-anion distances. Aside from qualitative discussions (Wollan, 1960), no non-empirical analysis of such indirect exchange interactions in spinel-like systems has been made. In what follows, we consider a detailed calculation for one of the mechanisms suggested before, on the basis of an appropriate model chosen.

In view of the large A-A distance and unfavourable angles, we shall disregard the study of the A-A interaction. As is supported by experimental results this interaction, in any way, is too feeble. The problem then is to select a model which includes the effect of both A-B and B-B interactions. Although we shall always keep the unit A-O-B₃ (with C_{3v} symmetry) in mind, we choose a still smaller unit, namely, A-O-B₂, which furnishes the appropriate model for describing both types of interactions. At times, while considering the symmetry of orbitals involved in the study, we shall refer to the complete unit having C_{3v} symmetry. If the O²⁻ ion in the unit A-O-B₂ was in the plane of A-B₂, the symmetry of A-O-B₂ would have been taken as C_{2v} . Since, O²⁻ is slightly below this plane, this symmetry is lost. However, we shall make use of some symmetry planes even for this unit in order to classify the orbitals and to study the nature of wavefunctions. The geometry of the unit is shown in Fig. 1.

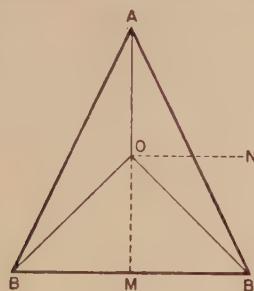


Fig. 1

3. THE WAVE FUNCTIONS OF THE CATION ELECTRONS

We consider one representative electron each from the three magnetic ions i.e., one at the tetrahedral, site A, and the other two at the octahedral sites B and B¹. Each electron is assumed to be coupled strongly by intraatomic spin dependent interaction while moving in the field of their respective ion cores. Only one type of magnetic ions are considered for simplicity with d^5 electronic configuration and in $^6S_{5/2}$ state e.g., Fe³⁺.

We denote the orbital functions of the electrons of the two octahedral cations by u_1 and u_2 and that of the tetrahedral cation by v . In the choice of the explicit forms of these orbitals, we shall be guided by their degree of overlap with the anion orbitals, and the splitting of the d orbitals in the crystal field. It is well known that in the cubic field due to octahedrally situated six surrounding ions the $3d$ level of the magnetic ion splits up into lower triplets (t_{2g}) and the upper doublets (e_g), the triplets being d_{xy} , d_{yz} and d_{zx} and the two doublets being $d_{2z^2-x^2-y^2}$ and $d_{x^2-y^2}$. When the cations are tetrahedrally surrounded by the anions, the situation is reversed and the triplets are higher than the doublets.

If the three cartesian axes are taken to be the lines joining the anion to the three octahedral cations, then the obvious choice for u_1 and u_2 would be one of the e_g orbitals, in particular, the d -function having axial symmetry with respect to the bonds BO and B'O (see Fig. 1). For v one can take the appropriate t_{2g} orbital. Any other choice of axes (e.g., A O as the z axis and x parallel to BB' and passing through O) would not make any difference in the calculations presented below in that the orbitals can be re-expressed by suitable transformations. Thus we assume the following behaviour of u_1 , u_2 and v under reflection in the plane AM normal to the figure (Fig. 1).

$$u_1 \longleftrightarrow u_2 \quad \text{and} \quad R_{AM}v = v$$

where R_{AM} denotes the corresponding operation. Switching over to the condition $R_{AM}v = -v$ would not bring about any difference in the physical arguments involved in the calculations.

Including the spin functions, we shall have eight Slater determinants for the three cation electron system. We shall choose such linear combinations of these which are eigenstates of the S^2 operator. We have one quartet and two doublet states. These are given below :

$$|^4\Phi_{od}(M_s = \frac{3}{2})\rangle_c = [u_1u_2v] \quad \dots \quad (3.1)$$

$$|^2\Phi_{od}(\frac{1}{2})\rangle_c = \{[u_1\bar{u}_2v] + [\bar{u}_1u_2v] - 2[u_1u_2\bar{v}]\} \mid \sqrt{6} \quad \dots \quad (3.2)$$

$$|^2\Phi_{ev}(\frac{1}{2})\rangle_c = \{[u_1\bar{u}_2v] - [\bar{u}_1u_2v]\} \mid \sqrt{2} \quad \dots \quad (3.3)$$

Here the bracket notation represents the usual Slater determinant multiplied by $(N!)^{-\frac{1}{2}}$ (in this case $(3!)^{-\frac{1}{2}}$). The orbitals without bar include up spin and with bar down spin functions of the electrons in them. The suffix c outside the kets refers it with respect to cation electrons and the suffixes od or ev denote that the states are odd or even under the operation R_{AM} .

The classification of the states with respect to the symmetry operation R_{AM} has the following advantage. The quartet $|^4\Phi_{od}\rangle_c$, of course, would represent the ferromagnetic state. The ferrimagnetic state $|^2\Phi_{od}\rangle_c$ represents the situation where the spins in A and B are antiparallel, while that of BB' are parallel. In effect, this would represent a dominant negative A-B interaction. The state $|^2\Phi_{ev}\rangle_c$, however, represents the reverse situation with antiparallel spins of BB' and parallel spins of AB. This represents the case with stronger B-B interaction. The picture remains incomplete unless the effect of anion electrons is included.

4. THE WAVE FUNCTIONS OF THE ANION ELECTRONS

Unlike our previous papers, where for anion electrons semilocalized orbitals are used, we shall follow a perturbation procedure right through in the present

formulation. We consider two anion electrons which play the dominant role in our mechanism. The appropriate $2p$ orbitals of the anion (e.g., O^{2-}) are no longer degenerate in the crystal field for the unit $A-O-B_3$ with C_{3v} symmetry. For the choice of axes along the three octahedral cations, the crystal field VC_{3v} gives rise to one non-degenerate orbital,

$$p_1(A_1) = \frac{1}{\sqrt{3}}(p_x + p_y + p_z) \quad \dots \quad (4.1)$$

belonging to A_1 representation of C_{3v} group and two degenerate orbitals, belonging to E representations i.e.,

$$\left. \begin{aligned} p_2(E) &= \frac{1}{\sqrt{2}}(p_x - p_y) \\ p_3(E) &= \frac{1}{\sqrt{6}}(2p_z - p_x - p_y) \end{aligned} \right\} \quad \dots \quad (4.2)$$

If, on the other hand, AO is taken as the z axis and ON as the x axis, it can be easily shown that p_z belongs to A_1 representation and its energy differs from the doubly degenerate orbitals p_x and p_y belonging to E representation. It is seen for both cases that the orbital belonging to A_1 representation has a larger overlap with the orbitals of the cation electrons.

We represent the zeroth order ground state for the anion system by considering the representative two electrons with coupled spins in the orbital belonging to A_1 representation. We denote this symbolically by ϕ . It may be added that for the restricted unit $A-O-B_2$ we shall replace $p_1(A_1)$ by

$$p_1 = (p_z + p_x)/\sqrt{2} \quad \dots \quad (4.3)$$

with OB as z axis and OB' as x in that the effect of p_y would be negligible. Thus our ϕ would represent p_1 as given by (4.3) or p_z depending on the choice of axes. In effecting the actual transformation the vector-like nature of the p orbitals should be taken into account.

The wave functions of the two anion electrons in the zeroth order ground state is expressed as

$$|{}^1\chi^{(0)}_{ev}\rangle_a = [\phi\bar{\phi}] \quad (4.4)$$

which is even under R_{AM} .

We defer the specific choice of excited orbitals until later sections and consider their effect in terms of some symmetry properties. It would suffice to consider the configurational interactions in terms of transitions to two types of orbitals, one even under R_{AM} and the other odd. They are respectively denoted by γ and η .

We have the following triplet states for the two anion electrons under consideration.

$$|{}^3\chi_{ev}>_a : \left. \begin{array}{l} [\phi\gamma] \\ \{[\phi\bar{\gamma}]+[\bar{\phi}\gamma]\} \\ [\bar{\phi}\bar{\gamma}] \end{array} \right\} | \sqrt{2} \quad \dots \quad (4.5)$$

$$|{}^3\chi_{od}>_a : \left. \begin{array}{l} [\phi\eta] \\ \{[\phi\bar{\eta}]+[\bar{\phi}\eta]\} \\ [\bar{\phi}\bar{\eta}] \end{array} \right\} | \sqrt{2} \quad \dots \quad (4.6)$$

Singlet states for the two anion electrons involving γ or η will have much higher energy than those described above and accordingly we omit them.

5. THE WAVE FUNCTIONS OF THE TOTAL SYSTEM

We first consider the zeroth order ground states of the total five electron and four centre system. The lowest state of the two anion electrons is $|{}^1\chi_{ev}>_a$ (cf. Eq. (4.4)] and hence the lowest ferromagnetic and two ferrimagnetic states are given by the products of (4.4) with (3.1), (3.2) and (3.3) respectively.

Ground states :

$$|{}^4\bar{\Psi}_{od}^{(\frac{1}{2})}> = ({}^4\Phi_{od}^{(\frac{1}{2})})_c ({}^1\chi_{ev}^{(0)})_a > = [u_1 u_2 v \phi \bar{\phi}] \quad \dots \quad (5.1)$$

$$\begin{aligned} |{}^2\bar{\Psi}_{od}^{(\frac{1}{2})}> &= ({}^2\Phi_{od}^{(\frac{1}{2})})_c ({}^1\chi_{ev}^{(0)})_a > \\ &= \{[u_1 \bar{u}_2 v \phi \bar{\phi}] + [\bar{u}_1 u_2 v \phi \bar{\phi}] - 2[u_1 u_2 \bar{v} \phi \bar{\phi}]\} | \sqrt{6} \end{aligned} \quad \dots \quad (5.2)$$

$$\begin{aligned} |{}^2\bar{\Psi}_{ev}^{(\frac{1}{2})}> &= ({}^2\Phi_{ev}^{(\frac{1}{2})})_c ({}^1\chi_{ev}^{(0)})_a > \\ &= \{[u_1 \bar{u}_2 v \phi \bar{\phi}] - [\bar{u}_1 u_2 v \phi \bar{\phi}]\} | \sqrt{2} \end{aligned} \quad \dots \quad (5.3)$$

A large number of excited states for the total system is possible. These are the products of the cation states (3.1), (3.2) and (3.3) and the excited triplet states of the anion, namely, (4.5) and (4.6). We shall write down only those states which have the appropriate symmetry corresponding to the respective zeroth order ferromagnetic and ferrimagnetic states. Others with different symmetry are of no consequence in that they do not interact with the corresponding ground states described by (5.1) to (5.3). The excited states involving transitions to γ and η type orbitals are given below :

Excited States

Quartets

$$\begin{aligned} |{}^4\bar{\Psi}_{od}^{\gamma_1(\frac{3}{2})}> &= \sqrt{\frac{2}{5}} | ({}^4\bar{\Phi}_{od}^{(\frac{1}{2})})_c ({}^3\chi_{cv}^{(1)})_a > - \sqrt{\frac{3}{5}} | ({}^4\bar{\Phi}_{od}^{\frac{9}{2}})_c ({}^3\chi_{ev}^{(0)})_a > \\ &= \{2([\bar{u}_1 u_2 v \phi \gamma] + [u_1 \bar{u}_2 v \phi \gamma] + [u_1 u_2 \bar{v} \phi \gamma]) \\ &\quad - 3([u_1 u_2 v \phi \bar{\gamma}] + [u_1 \bar{u}_2 v \bar{\phi} \gamma])\} | \sqrt{30} \end{aligned} \quad \dots \quad (5.4)$$

$$\begin{aligned}
 |^4\bar{\Psi}_{od}^{\gamma_2}(\frac{3}{2})\rangle &= |(^2\Phi_{od}^{(\frac{1}{2})})_c(^3\chi_{ev}^{(1)})_a\rangle \\
 &= \{2[u_1u_2\bar{v}\phi\gamma] - [u_1\bar{u}_2v\phi\gamma] - [\bar{u}_1u_2v\phi\gamma]\}|\sqrt{6} \quad \dots \quad (5.5)
 \end{aligned}$$

Doublets

$$\begin{aligned}
 |^2\bar{\Psi}_{od}^{\gamma_1}(\frac{1}{2})\rangle &= \sqrt{\frac{6}{18}} |(^2\bar{\Phi}_{od}^{(\frac{1}{2})})_c(^3\chi_{ev}^{(0)})_a\rangle - \sqrt{\frac{12}{18}} |(^2\bar{\Phi}_{od}^{(-\frac{1}{2})})_c(^3\chi_{ev}^{(1)})_a\rangle \\
 &= \{([u_1\bar{u}_2v\phi\bar{\gamma}] + [u_1\bar{u}_2v\bar{\phi}\gamma] + [\bar{u}_1u_2v\phi\bar{\gamma}] + [\bar{u}_1u_2v\bar{\phi}\gamma] \\
 &\quad - 2[u_1u_2\bar{v}\phi\bar{\gamma}] - 2[u_1u_2\bar{v}\bar{\phi}\gamma]) \\
 &\quad + (2[u_1\bar{u}_2\bar{v}\phi\gamma] + 2[\bar{u}_1u_2\bar{v}\phi\gamma] - 4[\bar{u}_1\bar{u}_2v\phi\gamma])\}|\sqrt{36} \quad \dots \quad (5.6)
 \end{aligned}$$

$$\begin{aligned}
 |^2\bar{\Psi}_{od}^{\gamma_2}(\frac{1}{2})\rangle &= \sqrt{\frac{3}{6}} |(^4\bar{\Phi}_{od}^{(\frac{3}{2})})_c(^3\chi_{ev}^{(-1)})_a\rangle - \sqrt{\frac{2}{6}} |(^4\bar{\Phi}_{od}^{(\frac{1}{2})})_c(^3\chi_{ev}^{(0)})_a\rangle \\
 &\quad + \sqrt{\frac{1}{6}} |(^4\bar{\Phi}_{od}^{(-\frac{1}{2})})_c(^3\chi_{ev}^{(1)})_a\rangle \\
 &= \{3[u_1u_2v\bar{\phi}\bar{\gamma}] - ([\bar{u}_1u_2v\phi\bar{\gamma}] + [\bar{u}_1u_2v\bar{\phi}\gamma] + [u_1\bar{u}_2v\phi\bar{\gamma}] \\
 &\quad + [u_1\bar{u}_2v\bar{\phi}\gamma] + [u_1u_2\bar{v}\phi\bar{\gamma}] + [u_1u_2\bar{v}\bar{\phi}\gamma] \\
 &\quad + ([\bar{u}_1\bar{u}_2v\phi\gamma] + [\bar{u}_1u_2\bar{v}\bar{\phi}\gamma] + [u_1\bar{u}_2\bar{v}\phi\gamma]))\}|\sqrt{18} \quad \dots \quad (5.7)
 \end{aligned}$$

$$\begin{aligned}
 |^2\bar{\Psi}_{ev}^{\gamma_1}(\frac{1}{2})\rangle &= \sqrt{\frac{2}{6}} |(^2\bar{\Phi}_{ev}^{(\frac{1}{2})})_c(^3\chi_{ev}^{(0)})_a\rangle - \frac{2}{\sqrt{6}} |(^2\bar{\Phi}_{ev}^{(-\frac{1}{2})})_c(^3\chi_{ev}^{(1)})_a\rangle \\
 &= \{[u_1\bar{u}_2v\phi\bar{\gamma}] + [u_1\bar{u}_2v\bar{\phi}\gamma] - [\bar{u}_1u_2v\phi\bar{\gamma}] - [\bar{u}_1u_2v\bar{\phi}\gamma] \\
 &\quad - 2[u_1\bar{u}_2\bar{v}\phi\gamma] + 2[\bar{u}_1u_2\bar{v}\phi\gamma]\}|\sqrt{12} \quad \dots \quad (5.8)
 \end{aligned}$$

Excited states involving transition to η type orbital.

Quartets :

$$\begin{aligned}
 |^4\bar{\Psi}_{od}^{\eta_1}(\frac{3}{2})\rangle &= |(^2\Phi_{od}^{(\frac{1}{2})})_c(^3\chi_{od}^{(1)})_a\rangle \\
 &= \{[u_1\bar{u}_2v\phi\eta] - [\bar{u}_1u_2v\phi\eta]\}|\sqrt{12} \quad \dots \quad (5.9)
 \end{aligned}$$

Doublets :

$$|^2\bar{\Psi}_{od}^{\eta_1}(\frac{1}{2})\rangle = \sqrt{\frac{2}{6}} |(^2\Phi_{od}^{(\frac{1}{2})})_c(^3\chi_{od}^{(0)})_a\rangle - \frac{2}{\sqrt{6}} |(^2\Phi_{od}^{(-\frac{1}{2})})_c(^3\chi_{od}^{(1)})_a\rangle \quad (5.10)$$

The explicit form for (5.10) is the same as (5.8) except that the orbital γ is replaced by η .

$$|^2\bar{\Psi}_{ev}^{\eta_1}(\frac{1}{2})\rangle = \sqrt{\frac{6}{18}} |(^2\Phi_{od}^{(\frac{1}{2})})_c(^3\chi_{od}^{(0)})_a\rangle - \sqrt{\frac{12}{18}} |(^2\Phi_{od}^{(-\frac{1}{2})})_c(^3\chi_{od}^{(1)})_a\rangle \quad \dots \quad (5.11)$$

$$\begin{aligned} \langle {}^2\bar{\Psi}_{ev} \eta_2 (\frac{1}{2}) \rangle &= \sqrt{\frac{3}{8}} \langle {}^4\Phi_{od} (\frac{3}{2})_c ({}^3\chi_{od}^{(-1)})_a \rangle - \sqrt{\frac{3}{8}} \langle {}^4\Phi_{od} (\frac{1}{2})_c ({}^3\chi_{od}^{(0)})_a \rangle \\ &+ \sqrt{\frac{1}{8}} \langle {}^4\Phi_{od} (-\frac{1}{2})_c ({}^3\chi_{od}^{(1)})_a \rangle \quad \dots \quad (5.12) \end{aligned}$$

The explicit forms of (5.11) and (5.12) are respectively obtained by putting the orbital η in place of γ in (5.6) and (5.7).

6. EVALUATION OF THE ENERGY MATRIX

The Hamiltonian (in atomic units $e = \hbar = m = 1$) is

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i>j} \frac{1}{r_{ij}} \quad \dots \quad (6.1)$$

where $V(r_i)$ is the potential acting on the i th electron due to the four nuclei and all other electrons except the five under consideration. The energy matrix of the Hamiltonian within the manifold described in the previous section is given below :

Diagonal elements

Ground states :

$$\langle {}^4\bar{\Psi}_{od} | H | {}^4\bar{\Psi}_{od} \rangle = [Q_0 - J(u_1 u_2) - 2J(u_1 v) - 2J(u_1 \phi) - J(v \phi)] \quad \dots \quad (6.2)$$

$$\langle {}^2\bar{\Psi}_{od} | H | {}^2\bar{\Psi}_{od} \rangle = [Q_0 - J(u_1 u_2) + J(u_1 v) - 2J(u_1 \phi) - J(v \phi)] \quad \dots \quad (6.3)$$

$$\langle {}^2\bar{\Psi}_{ev} | H | {}^2\bar{\Psi}_{ev} \rangle = [Q_0 + J(u_1 u_2) - J(u_1 v) - 2J(u_1 \phi) - J(v \phi)] \quad \dots \quad (6.4)$$

Excited states involving transition to γ type orbital.

Quartets :

$$\begin{aligned} \langle {}^4\bar{\Psi}_{od} \gamma_1 | H | {}^4\bar{\Psi}_{od} \gamma_1 \rangle &= [Q_\gamma - J(u_1 u_2) - 2J(u_1 v) - J(\phi \gamma) \\ &- \frac{1}{2}\{J(u_1 \phi) + J(u_1 \gamma)\} - \frac{1}{2}\{J(v \phi) + J(v \gamma)\}] \quad \dots \quad (6.5) \end{aligned}$$

$$\begin{aligned} \langle {}^4\bar{\Psi}_{od} \gamma_2 | H | {}^4\bar{\Psi}_{od} \gamma_2 \rangle &= [Q_\gamma - J(u_1 u_2) + J(u_1 v) - J(\phi \gamma) \\ &- \frac{5}{2}\{J(u_1 \phi) + J(u_1 \gamma)\} - \frac{1}{2}\{J(v \phi) + J(v \gamma)\}] \quad \dots \quad (6.6) \end{aligned}$$

Doubllets :

$$\begin{aligned} \langle {}^2\bar{\Psi}_{od} \gamma_1 | H | {}^2\bar{\Psi}_{od} \gamma_1 \rangle &= [Q_\gamma - J(u_1 u_2) + J(u_1 v) - J(\phi \gamma) \\ &+ \frac{1}{2}\{J(u_1 \phi) + J(u_1 \gamma)\} - \frac{5}{8}\{J(v \phi) + J(v \gamma)\}] \quad \dots \quad (6.7) \end{aligned}$$

$$\begin{aligned} \langle {}^2\bar{\Psi}_{od} \gamma_2 | H | {}^2\bar{\Psi}_{od} \gamma_2 \rangle &= [Q_\gamma - J(u_1 u_2) - 2J(u_1 v) - J(\phi \gamma) \\ &+ \frac{1}{2}\{2J(u_1 \phi) + 2J(u_1 \gamma) + J(v \phi) + J(v \gamma)\}] \quad \dots \quad (6.8) \end{aligned}$$

$$\begin{aligned} \langle {}^2\bar{\Psi}_{ev}^{\gamma_1} | H | {}^2\bar{\Psi}_{ev}^{\gamma_1} \rangle &= [Q_\gamma + J(u_1 u_2) - J(u_1 v) - J(\phi \gamma) \\ &\quad - J(u_1 \phi) - J(u_1 \gamma) + \frac{1}{2}\{J(v\phi) + J(v\gamma)\}] \end{aligned} \quad \dots \quad (6.9)$$

For transition to η type orbital.

Quartet :

$$\begin{aligned} \langle {}^4\bar{\Psi}_{od}^{\eta_1} | H | {}^4\bar{\Psi}_{od}^{\eta_1} \rangle &= [Q_\eta + J(u_1 u_2) - J(u_1 v) - J(u_1 \phi) - J(u_1 \eta) \\ &\quad - J(v\phi) - J(v\eta) - J(\phi\eta)] \end{aligned} \quad \dots \quad (6.10)$$

Doubles :

$$\langle {}^2\bar{\Psi}_{od}^{\eta_1} | H | {}^2\bar{\Psi}_{od}^{\eta_1} \rangle = \text{as in (6.9) with } \gamma \text{ replaced by } \eta. \quad \dots \quad (6.11)$$

$$\langle {}^2\bar{\Psi}_{ev}^{\eta_1} | H | {}^2\bar{\Psi}_{ev}^{\eta_1} \rangle = \text{as in (6.7) with } \gamma \text{ replaced by } \eta. \quad \dots \quad (6.12)$$

$$\langle {}^2\bar{\Psi}_{ev}^{\eta_2} | H | {}^2\bar{\Psi}_{ev}^{\eta_2} \rangle = \text{as in (6.8) with } \gamma \text{ replaced by } \eta. \quad \dots \quad (6.13)$$

The symbols occurring in the right hand side of Eqns. (6.2) to (6.13) stand for the following :

$$\begin{aligned} Q_0 &= \{2\epsilon_u + \epsilon_v + 2\epsilon_\phi + K(u_1 u_2) + 2K(u_1 v) + 4K(u_1 \phi) \\ &\quad + 2K(v\phi) + K(\phi\phi)\} \end{aligned} \quad \dots \quad (6.14)$$

$$\begin{aligned} Q_a &= \{2\epsilon_u + \epsilon_v + \epsilon_\phi + \epsilon_a + K(u_1 u_2) + 2K(u_1 v) + 2K(u_1 \phi) \\ &\quad + 2K(u_1 a) + K(v\phi) + K(va) + K(\phi a)\} \end{aligned} \quad \dots \quad (6.15)$$

$$\left. \begin{aligned} K(ab) &\equiv \langle ab | g_{12} | ab \rangle, \text{ the coulomb integral} \\ J(ab) &\equiv \langle ab | g_{12} | ba \rangle, \text{ the exchange integral} \end{aligned} \right\} \quad \dots \quad (6.16)$$

[see also (6.24)]

and $\epsilon_a \equiv \langle a | -\frac{1}{2}\nabla^2 + V | a \rangle$ the one electron term. $\dots \quad (6.17)$

In writing down the final expressions we have made use of the conditions $u_1 \longleftrightarrow u_2$ under R_{AM} . It is to be noted that the diagonal matrix elements (6.2) to (6.4) for the zeroth order ground states are degenerate if we neglect the relatively feeble direct exchange integrals such as $J(u_1 u_2)$ and $J(u_1 v)$. It is essential, therefore, to study the interaction of these states with the corresponding excited states in order to determine the effective coupling on the basis of the present mechanism. The off-diagonal matrix elements will be described now.

Off-diagonal elements

(i) Involving transition to γ .

$$\langle {}^4\bar{\psi}_{od} | H | {}^4\bar{\psi}_{od}^{\gamma_1} \rangle = -\sqrt{\frac{5}{6}} \{ \langle u_1 \gamma | g_{12} | \phi u_1 \rangle + \langle u_2 \gamma | g_{12} | \phi u_2 \rangle \\ + \langle v \gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.18)$$

$$\langle {}^4\bar{\psi}_{od} | H | {}^4\bar{\psi}_{od}^{\gamma_2} \rangle = -\sqrt{\frac{1}{6}} \{ \langle u_1 \gamma | g_{12} | \phi u_1 \rangle + \langle u_2 \gamma | g_{12} | \phi u_2 \rangle \\ - 2 \langle v \gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.19)$$

$$\langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\gamma_1} \rangle = -\sqrt{\frac{1}{6}} \{ 2 \langle u_1 \gamma | g_{12} | \phi u_1 \rangle + 2 \langle u_2 \gamma | g_{12} | \phi u_2 \rangle \\ - \langle v \gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.20)$$

$$\langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\gamma_2} \rangle = -\sqrt{\frac{1}{6}} \{ \langle u_1 \gamma | g_{12} | \phi u_1 \rangle + \langle u_2 \gamma | g_{12} | \phi u_2 \rangle \\ - 2 \langle v \gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.21)$$

$$\langle {}^2\bar{\psi}_{ev} | H | {}^2\bar{\psi}_{ev}^{\gamma_1} \rangle = \frac{3}{\sqrt{6}} \langle v \gamma | g_{12} | \phi v \rangle \quad \dots \quad (6.22)$$

(ii) For interactions with excited states involving transition to η like orbital, we have one composite expression for the off-diagonal elements, i.e.,

$$\langle {}^4\bar{\psi}_{od} | H | {}^4\bar{\psi}_{od}^{\eta_1} \rangle = \langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\eta_1} \rangle = \langle {}^2\bar{\psi}_{ev} | H | {}^2\bar{\psi}_{ev}^{\eta_1} \rangle \\ = \frac{1}{\sqrt{2}} \{ \langle {}^2\bar{\psi}_{ev} | H | {}^2\bar{\psi}_{ev}^{\eta_2} \rangle \} = \frac{1}{\sqrt{2}} \{ \langle u_1 \eta | g_{12} | \phi u_1 \rangle \\ - \langle u_2 \eta | g_{12} | \phi u_2 \rangle \} \quad \dots \quad (6.23)$$

The notations like $\langle ab | g_{12} | cd \rangle$ in the diagonal and off-diagonal elements represents the integral

$$\int \int a^*(\mathbf{r}_1) b^*(\mathbf{r}_2) \frac{1}{r_{12}} c(\mathbf{r}_1) d(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad \dots \quad (6.24)$$

7. STUDY OF INTERACTION BY PERTURBATION PROCEDURE

If we examine the diagonal matrix elements of the excited states i.e., Eqns. (6.5) to (6.13) it is seen that the term like $Q(a)$ (explicitly given by (6.15)) is common to all the expressions for transition to 'a' type orbital. Since this contains terms such as the one electron and the coulomb integrals $K(ab)$, it is by far the dominant

term as compared to those involving the exchange integrals $J(ab)$, which are relatively very negligible. We can thus safely use the approximation.

$${}^4E_a \simeq {}^2E_a = E_a' \quad \dots \quad (7.1)$$

where E' represents the mean energy of the excited states involving 'a' orbital. Further, we use the notation

$$E_a = E_a' - E_0 \quad \dots \quad (7.2)$$

where

$${}^4E_0 = {}^2E_0 = E_0$$

i.e., the degenerate energy of the zeroth order ground quartet and doublet states.

As shown in our previous papers (Koide, Sinha and Tanabe, 1959; Sinha and Koide, 1960), the spin dependent energy depressions of the various lower states, within the framework of the present formalism, appears in the second order term of the perturbation treatment. This is expressed as

$$\begin{aligned} \delta E_n &= \sum_n \langle 0 | H | n \rangle \langle n | H | 0 \rangle / (E_n - E_0) \\ &\approx (E_a)^{-1} \sum_n \langle 0 | H | n \rangle \langle n | H | 0 \rangle \quad \dots \quad (7.3) \end{aligned}$$

using (7.1) and (7.2).

It is expedient to consider certain symmetry situations before giving the explicit expressions for the energy depressions of the various quartet and doublet states based on (7.3).

Under the operation R_{AM} we take, as pointed before, $u_1 \longleftrightarrow u_2$; the behaviour of v either as even or odd function, would not affect the hybrid exchange integrals $\langle vb | g_{12} | cv \rangle$ occurring in the off-diagonal elements. Further, under the operation R_{ON} i.e., reflection on the plane ON normal to the Fig. 1., ϕ is expected to behave as $R_{ON}\phi = -\phi$ because ϕ is either a p_z orbital or a combination of p orbitals by (4.3) depending on the choice of axes. As noted before, for η we take $R_{AM}\eta = -\eta$. In the case of γ , we consider two possibilities.

(a) $R_{AM}\gamma = \gamma$ (always)

(b) i) $R_{ON}\gamma = \gamma$ or ii) $R_{ON}\gamma = -\gamma$.

We shall consider the energy depressions of the states with the condition $R_{ON}\gamma = \gamma$; then we have only to show that the lowest available excited orbital of γ type has this symmetry.

We now consider the explicit expression for the energy depressions of the zeroth order ground states (5.1), (5.2) and (5.3) due to the second order perturba-

tion terms as contained in (7.3), under various conditions. The respective depressions will be symbolically denoted by δQ , δD_1 and δD_2 . These are dealt with casewise.

Case I. (Perturbation by excited states involving transition to γ type orbital).

It is convenient to introduce the following abbreviations

$$\langle u_1\gamma | g_{12} | \phi u_1 \rangle \equiv u_1 J_{\gamma\varphi}; \quad \langle v\gamma | g_{12} | \phi v \rangle \equiv v J_{\gamma\varphi} \text{ etc.} \quad \dots \quad (7.4)$$

We also note that $u_2 J_{\gamma\varphi} = u_1 J_{\gamma\varphi}$ because of the symmetry $u_1 \rightleftharpoons u_2$ under R_{AM} and that $R_{ON} v J_{\gamma\varphi} = -v J_{\gamma\varphi}$. Thus making use of these conditions in the appropriate off-diagonal elements, the depressions of the various states are expressed below :

$$\delta Q : \{ \frac{5}{6} |(2u_1 J_{\gamma\varphi} - v J_{\gamma\varphi})|^2 + \frac{1}{6} |(2u_1 J_{\gamma\varphi} + 2v J_{\gamma\varphi})|^2 \} / E_\gamma \quad \dots \quad (7.5)$$

$$\delta D_1 : \{ \frac{1}{6} |(4u_1 J_{\gamma\varphi} + v J_{\gamma\varphi})|^2 + \frac{2}{6} |(2u_1 J_{\gamma\varphi} + 2v J_{\gamma\varphi})|^2 \} / E_\gamma \quad \dots \quad (7.6)$$

$$\delta D_2 : \frac{1}{6} \{ 9 |v J_{\lambda\varphi}|^2 \} / E_\gamma \quad \dots \quad (7.7)$$

It follows, therefore, that

$$\delta Q - \delta D_1 = 6 |u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}| / E_\gamma \quad \dots \quad (7.8)$$

$$\delta Q - \delta D_2 = \{ -4 |u_1 J_{\gamma\varphi}|^2 + 2 |u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}| \} / E_\gamma \quad \dots \quad (7.9)$$

$$\delta D_2 - \delta D_1 = \{ 4 |u_1 J_{\gamma\varphi}|^2 + 4 |u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}| \} / E_\gamma \quad \dots \quad (7.10)$$

It is easily seen from the above equations that the depression of the D_1 is maximum and it is the lowest of the three states for transition to the γ type orbital. D_2 will probably lie above Q .

Case II. (Involving transition to η type orbital). Noting, $R_{AM} u_1 J_{\eta\varphi} = -u_1 J_{\eta\varphi}$, the depressions of the various states are :

$$\delta Q : 2 |u_1 J_{\eta\varphi}|^2 / E_\eta \quad \dots \quad (7.11)$$

$$\delta D_1 : 2 |u_1 J_{\eta\varphi}|^2 / E_\eta \quad \dots \quad (7.12)$$

$$\delta D_2 : \{ 2 |u_1 J_{\eta\varphi}|^2 + 4 |u_1 J_{\eta\varphi}|^2 \} / E_\eta \quad \dots \quad (7.13)$$

$$\text{Hence} \quad \delta Q - \delta D_1 = 0 \quad \dots \quad (7.14)$$

$$\text{and} \quad \delta Q - \delta D_2 = 4 |u_1 J_{\eta\varphi}|^2 / E_\eta \quad \dots \quad (7.15)$$

In this case, D_2 is the lowest state and Q and D_1 lie above and are degenerate. Of the two cases discussed above the fact as to which will dominate would depend on the magnitude of E_γ and E_η as well as the hydrid exchange integrals $a J_{bc}$ involved. However, it is more appropriate to discuss the case when they are of the same magnitude.

Case III. (The energies of γ and η are equal. We can use the approximation $E_\gamma = E_\eta = E$.) Then we have

$$\delta Q - \delta D_1 = 6|u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}| / E \quad \dots \quad (7.16)$$

$$\begin{aligned} \delta Q - \delta D_2 &= \{4|u_1 J_{\eta\varphi}|^2 - 4|u_1 J_{\gamma\varphi}|^2 + 2|u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}|\} / E \\ &\approx 2|u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}| / E \end{aligned} \quad \dots \quad (7.17)$$

$$\begin{aligned} \delta D_2 - \delta D_1 &= \{4|u_1 J_{\gamma\varphi}|^2 - 4|u_1 J_{\eta\varphi}|^2 + 4|u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}|\} / E \\ &\approx 4|u_1 J_{\gamma\varphi}| |v J_{\gamma\varphi}| / E \end{aligned} \quad \dots \quad (7.18)$$

assuming that $|u_1 J_{\gamma\varphi}| \approx |v_1 J_{\eta\varphi}|$.

If this was the case, then D_1 would be the lowest state, D_2 and Q representing the higher states in respective orders. It may be mentioned again that the ferrimagnetic state D_1 , represents the situation where negative A-B coupling dominates over B-B; D_2 represents the reverse situation. The above analysis shows that the ferro-magnetic state Q is least likely, in agreement with observed cases.

We shall, however, proceed further and investigate deeper into the specific nature of the excited orbitals γ and η available in actual crystals of magnetic spinels and the like systems. After assessing the relative energies of the available excited orbitals, and the magnitude of the hybrid exchange integrals ($^a J_{bc}$), a semi-quantitative discussion of the effective coupling in these systems will be given and compared with results.

8. APPLICATION TO THE REAL SYSTEMS

In order to have a semiquantitative discussion of the model and ideas developed in the preceding sections as related to spinel-like systems, we shall select a typical representative. Simple examples are $\text{Mn}[\text{Fe}_2]\text{O}_4$ or $\gamma\text{-Fe}_2\text{O}_3$, in which all the cations have d^5 configuration and can be assumed to exist in $^6S_{5/2}$ state.

The first problem is the identification of γ and η type excited orbitals among the lowest available orbitals in the actual crystals. We classify these and ascertain their relative energies with respect to the full unit—A-O-B₃—having C_{3v} symmetry. In discussing the excited orbitals permissible for this point symmetry group, we shall be guided, as before, (Koide, Sinha and Tanabe, 1959), by two models. First we consider the “excitation model” which involves the transition of an electron to the lowest excited orbitals of the anion under the influence of the crystal field of the appropriate symmetry. Second is the charge “transfer model” and describes transitions to such linear combinations of the empty cation orbitals which form base functions of the irreducible representations of the point symmetry group. The lowest lying among these are, of course,

most effective in the transition process (virtual in the present case) being considered here. It may be added that from group theoretical point of view both models represent the same orbitals expressed in slightly different ways of approximations. They should better be termed as localized crystal orbitals.

The excited orbitals of O^{2-} that may be considered on the basis of the "excitation model" are $3s$, $3p$ and $3d$. In order to have a rough estimate of the relative energy scale for these, we consider the effect of the four cations in the unit A-O-B₃ (point symmetry C_{3v}) treated as point charges, as well as the twelve oxygen ion neighbours (treated not as point charges but ions with a distribution of charge).

The calculation is carried out by the usual method of crystal field theory (Bethe, 1929; Moffit and Ballhausen, 1956) where the potential is expanded in a series of spherical harmonics, the presence or absence of the terms being governed by the point symmetry group and certain group theoretical ideas. The matrix elements of the potential, thus expressed, were calculated by using the equivalent operator method (Bleaney and Stevens, 1953). The splittings of the orbital levels are proportional to $\langle r^2 \rangle / R^2$, $\langle r^4 \rangle / R^4$ etc., depending on whether the orbital is p -type or d -type. Here 'r' is the orbital radius and R is the distance of the neighbour in question.

A knowledge of the radial part of the respective wave-functions is needed; however, it is very hard to determine this non-empirically. One can, at best, make a plausible approximation. From the work on excitons for certain systems (Knox and Inchauspe, 1959), it is known that, in the excitation model (Dexter, 1951; 1957) the majority of the charge is confined within the equivalent sphere with its centre at the anion and the surface extending upto the cation centres. Keeping this fact in mind we choose the radial part of the wave-function by the following tentative method.

For example for the $3d$ orbital, we assume that the maximum of the wave-function lies midway between the anion and the cation i.e., for the present case approximately at 2 a.u. distance from the oxygen centre.

In view of the approximations used, it would serve no purpose to give here the details of the calculation. We only enumerate the rough results. Thus, with AO as the z axis and ON as the x axis, we get the following energy sequence :

$$3d_{z^2} < 3d_{xz} = 3d_{yz} \leq 3p_z < 3s < 3p_x = 3p_y < 3d_{(x^2-y^2)} = 3d_{xy}$$

The energy of the $3d_{z^2}$ is lowered by about 6 e.v. with respect to the continuum. It would therefore lie below the conduction band. However, one cannot place too much reliance on the above figure. The important thing is the derived energy sequence and that on the excitation model, a proper choice for γ would be $3d_{z^2}$ orbital and for η $3d_{xz}$. (A different choice of axes will not alter the essen-

tial features; the orbitals will then be the appropriate linear combinations which preserve the symmetry and the sequence). It may be noted, in passing, that $3d_{z^2}$ as γ and $3d_{xz}$ as η satisfy the requisite requirements taken into account in section 7.

We now turn to the charge transfer model in which γ or η are to be constituted out of a linear combination of empty cation orbitals. For the cations considered, we take the $4s$ or orbital or an sp hybrid of the $4s$ and $4p$ orbitals of the respective action having maximum charge density pointing towards the anion and having axial symmetry. We denote them (for the unit A-O-B₃) by σ_t , σ_1 , σ_2 and σ_3 respectively. They form base functions of a reducible representation of dimension 4 for the C_{3v} group. This can be decomposed into the various irreducible representations (for the group theoretical nomenclatures see Landau and Lifshitz, 1958). Thus :

$$\chi\{\Gamma(R)\} = 2\chi(A_1) + \chi(E) \quad \dots \quad (8.1)$$

Accordingly, we have the following combinations :

$$\left. \begin{array}{l} \psi_1(A_1) = \{a_t\sigma_t + a(\sigma_1 + \sigma_2 + \sigma_3)\}/(\text{Normalization}) \\ \psi_2(A_1) = \{a_t\sigma_t - a(\sigma_1 + \sigma_2 + \sigma_3)\}/(\text{Normalization}) \end{array} \right\} \quad \dots \quad (8.2)$$

$$\left. \begin{array}{l} \psi_3(E) = (\sigma_1 - \sigma_2)/\sqrt{2} \\ \psi_4(E) = (\sigma_1 + \sigma_2 - 2\sigma_3)/\sqrt{6} \end{array} \right\} \quad \dots \quad (8.3)$$

Among these some are of no physical interest for the unit A-O-B₂ (Cf. Fig. 1) and we consider only three in the following approximate forms.

$$\psi_a = [\sigma_t + (\sigma_1 + \sigma_2)]/\sqrt{3} \quad \dots \quad (8.4)$$

$$\psi_b = [\sigma_t - (\sigma_1 + \sigma_2)]/\sqrt{3} \quad \dots \quad (8.5)$$

$$\psi_c = [\sigma_1 - \sigma_2]/\sqrt{2} \quad \dots \quad (8.6)$$

Now ψ_c is orthogonal to ϕ ; however, ψ_a and ψ_b are not orthogonal to it. It can be easily seen that the overlap integral of ψ_b with ϕ is much higher than that of ψ_a with ϕ . Thus, the energy of ψ_b is pushed higher up due to mixing with ϕ and the hybrid exchange integral involving it would also be negligible. We can, therefore, safely disregard the effect of ψ_b . Finally, we select ψ_a and ψ_c for γ and η respectively. Since the non-orthogonality of ψ_a with ϕ is negligible, the orbital energies of ψ_a and ψ_c are expected to be nearly equal. Further, the hybrid exchange integrals involving ψ_a and ψ_c will not differ much. This situation leads to the case III dealt with in the Section 7.

It may be emphasised that it is difficult to determine as to which of the two models described above furnish the lowest lying excited orbitals. Since

group-theoretically they are so akin, we shall adopt that model for a semi-quantitative estimate which appeals to our chemical intuition. Accordingly, we choose the charge transfer model and identify γ with ψ_a and η with ψ_e .

The arguments of case III, Section 7 shows that the doublet state D_1 , which represents the state with antiparallel spins in A-B and parallel in B-B lies lowest. D_2 , representing the reverse situation, lies between the quartet Q and D_1 . If we consider the energy level in such a manner that Q represents the zero level, then (7.16) gives the position of D_1 . In the following we give the estimate for the difference $Q-D_1$ in terms of ψ_a and ψ_e i.e., equations (8.4) and (8.6). Thus we have

$$Q-D_1 = 6\{|\langle u_1\psi_a | g_{12} | \phi u_1 \rangle| + |\langle v\psi_a | g_{12} | \phi v \rangle|\}/E \\ \approx 2\{|\langle u_1\sigma_1 | g_{12} | \phi u_1 \rangle| + |\langle v\sigma_2 | g_{12} | \phi v \rangle|\}/E \quad \dots \quad (8.7)$$

Further, we use p_1 for ϕ , namely $p_1 = \frac{1}{\sqrt{2}}(p_z + p_x)$. The hydrid exchange

integrals of the type $\langle u_1\sigma | g_{12} | p_z u_1 \rangle$ have been evaluated in the previous paper (Koide, Sinha and Tanabe, 1959) for similar cations and anions. These are of the order of 0.01 a.u. or 0.27 e.v. for the separations involved in spinels. For determining $E \sim (E_a - E_o)$, the ionization potential and electron affinity data for the cation and anions were respectively used. The order is of about 1 a.u. However, for the present purpose, we shall use the range 0.5 to 1.5, a.u.. Using these values the difference $\Delta E \equiv Q-D_1$ is set out in Table 1.

TABLE I

E a.u.	ΔE	
	a.u.	°K
0.5	4×10^{-4}	125
1.0	2×10^{-4}	62.5
1.5	1.33×10^{-4}	42

A reasonable estimate for $(Q-D_1)$ pertaining to the systems such as Mn Fe₂O₄ would be around 50°K. The above is for a single representative electron from each cation. No attempt is made to relate this difference with the Curie temperature of the ferrites.

9. DISCUSSION

The purpose of the analysis presented in the foregoing sections has been to explore the nature of indirect exchange interaction for ferrospinels on the basis of the mechanism proposed. The stability of the ferromagnetic and the

two ferrimagnetic states have been studied. It emerges from these considerations that the ferrimagnetic state, symbolized, by D_1 is most stable. In contrast, the ferromagnetic state is least stable. This conclusion is in agreement with Neel's assumption and also the observed situation in most ferrospins where the negative A-B interaction is the most dominant effect (Gorter, 1954).

It may be pointed, however, that the state symbolised by D_2 (i.e., where B-B are antiparallel and A-B parallel), may become important under certain conditions. If the situation as discussed in Case III of Section 7, prevails, D_2 is more stable compared to the ferromagnetic state Q . However, to ascertain as to when it dominates over D_1 also, a precise knowledge of the excited orbitals is needed. It seems probable that D_2 may become most stable when the cation at the tetrahedral site is in a low spin state as compared to both the cations at the octahedral sites.

This paper does not assess the importance of this mechanism as compared to others. The greatest difficulty for all mechanisms lies in getting an accurate idea of the wave functions of electrons in crystals. Non-empirical calculations are obviously formidable. It is hoped that experiments may eventually resolve some of these difficulties.

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A NOTE ON THE CROSS-SECTION OF THE LUMINOUS DISCHARGE CHANNEL IN A GLOW DISCHARGE

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ABSTRACT. The variation in the cross-section x and the H.W.R. of a luminous discharge channel has been studied for different points in the cathode dark space of a glow discharge in hydrogen and air. Results show that,

- (1) the cross-section x reaches a minimum value at some distance Z in front of the cathode,
- (2) the value of the minimum cross-section as well as its location in the cathode dark space is a function of the pressure,
- (3) both the H.W.R. and x decrease with decreasing pressure for the range 400–252 microns to 100–150 microns. For lower pressures the variation of the two parameters is opposite in character.

INTRODUCTION

In a previous paper (Chiplonkar *et al.*, 1957) it had been shown that significant changes occur, with decrease in pressure, in the cross section as well as the radial intensity distribution of the luminous discharge channel of a glow discharge in air, mostly in the abnormal regime of the discharge. Similar changes were observed when observations were made on the channel at different points in the cathode dark space. At low pressures, when these changes are most pronounced, it was shown that the channel starts with a large cross-section, with a radial distribution of the flat maximum type (observed by Chaudhri and Baqui, 1952) and shows a progressive decrease in the cross-section as it proceeds towards the cathode. At the same time the radial distribution changes into an approximately Gaussian form (Chiplonkar, 1940 and 1947; Kamke 1950). These changes are to be expected and are in general agreement with the theory of Kamke. An important observation made by us that there is an increase in the cross-section of the channel in the immediate vicinity of the cathode, suggested a more detailed investigation of this interesting aspect of the problem which it is the object of the present paper to report.

2. EXPERIMENTAL RESULTS

The variation in the radial intensity distribution in the discharge channel was studied as before¹ (Chiplonkar, *et al.*, 1957) at various distances in the

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cathode dark space, extending the observation in some cases to points in the negative glow for discharge in air (voltages 0.68-9.80 KV, pressure 252-52 microns, current = 1.0 mA) and hydrogen (Voltages 0.20-9.83 KV, pressures 400-40 microns, current = 1.0 mA). For the above conditions electrical oscillations were not present in the discharge tube.

Following the procedure used previously, the experimental results are discussed with the help of the following parameters.

x = width of the axial region of the channel over which the intensity is constant

Z = distance of the channel from the cathode

d = D.S.L. = length of the cathode dark space

H.W.R. = half width radius for the total radial distribution as measured directly from the microphotometer curves.

A few typical individual observations are given in Tables I-III and Fig. 1, while the final results are presented in Table IV.

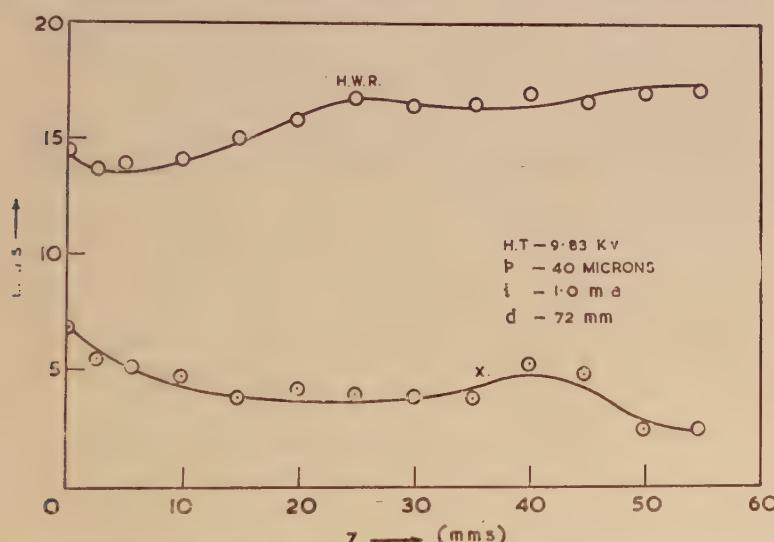


Fig. 1. Variation in the value of x and H.W.R. with Z for discharge in hydrogen.

3. DISCUSSION

The value of x and the half width radius (H.W.R.) can be taken as an adequate measure of the localisation of the discharge channel. An increase in the localisation being equivalent to a decrease in both the cross-section parameter x and the H.W.R. for the distribution. It will be noticed that in the case of all the observations reported here, the cross-section x of the discharge channel attains a minimum value for some point in front of the cathode. The variation of x_0 , the value of the cross section at the cathode, and of the minimum value

TABLE I
Discharge in air

$H-T = 6.14 \text{ KV}$, $i = 1.0 \text{ mA}$		$p = 53 \text{ microns}$	$d = 50 \text{ mm}$
$Z(\text{mm})$	$x(\text{mm})$	$H.W.R.(\text{mm})$	
0.0	07.4	16.9	
3.0	05.2	14.1	
8.0	05.1	13.9	
15.0	04.6	14.0	
25.0	04.3	14.6	
30.0	04.1	16.5	
35.0	04.8	16.9	
40.0	04.7	16.8	
45.0	04.7	16.5	
50.0	05.5	17.0*	

TABLE II
Discharge in hydrogen

$H-T = 0.84 \text{ KV}$, $i = 1.0 \text{ mA}$		$p = 155 \text{ microns}$	$d = 22 \text{ mm}$
$Z(\text{mms})$	$x(\text{mms})$	$H.W.R.(\text{mms})$	
0.0	14.0	9.2	
3.0	13.9	14.2	
6.0	13.0	11.1	
9.0	12.0	12.0	
12.0	12.4	16.9	
15.0	12.6	16.8	
18.0	13.2	11.4	
21.0	15.1	13.4	
23.0	17.6	17.0*	

TABLE IV

H^T (KV)	p (microns)	d (mm)	At cathode		At D.S.I. $Z = \frac{d}{x_d}$ x_d (mm) (H.W.R.) (mm)	x_{min} value of x (mm)	Position of x_{min} (mm.)	Minimum value of H.W.R.(mm.)	Position of H.W.R. min. (mm.)
			$Z = 0$	x_0 (mm) (H.W.R.) (mm)					
0.68	205	10	26.2	16.4	~	27	16.4	20.0	6.0
1.18	100	18	15.8	10.7	~	12	17.0	9.6	14.0
1.96	73	30	13.8	—	—	15.6	17.0	12.0	15.0
3.94	58	42	11.0	12.8	~	10	17.0	7.6	20.0
6.14	53	50	7.4	16.9	5.5	17.0	4.1	30.0	12.8
9.80	52	54	9.8	15.0	—	—	3.9	15.0	0.0
Discharge in hydrogen									
0.20	400	10	27.1	15.4	17.0	17.0	15.3	6.0	15.4
0.84	155	22	14.0	9.2	17.6	17.0	12.0	9.0	9.2
2.03	81	40	10.1	12.8	12.0	17.0	5.7	25.0	11.4
4.14	57	54	4.6	8.8	4.1	—	2.1	25.0-30.0	6.8
7.28	45	65	7.6	17.0	—	—	4.1	30.0	12.8
9.83	40	72	7.2	14.6	—	—	3.9	15.0	13.6

TABLE III
Discharge in hydrogen

$H.T. = 4.14 \text{ KV}$	$i = 1.0 \text{ mA}$	$p = 57 \text{ microns}$	$d = 54 \text{ mm.}$
$Z(\text{mm})$	$x(\text{mm})$	$H.W.R.(\text{mm})$	
0.0	4.6	8.8	
3.0	4.0	9.3	
6.0	3.9	10.5	
10.0	3.6	10.8	
15.0	3.5	9.4	
20.0	2.7	7.6	
25.0	2.1	7.3	
30.0	2.1	6.8	
35.0	2.5	7.5	
40.0	2.7	—	
45.0	3.2	—	
50.0	3.1	—	
55.0	4.1	—	

* Radius of the discharge tube $\sim 17.0 \text{ mm.}$

of x with pressure in the case of the two cases, shown in Fig. 2, are observed to be quite similar. Both of them show a minimum value for values of $p \sim 50$ microns. That there is a significant change in the state of the discharge at this pressure is indicated by Fig. 3 which shows the variation in the location of the minimum, with the pressure in the discharge tube. In the high pressure region

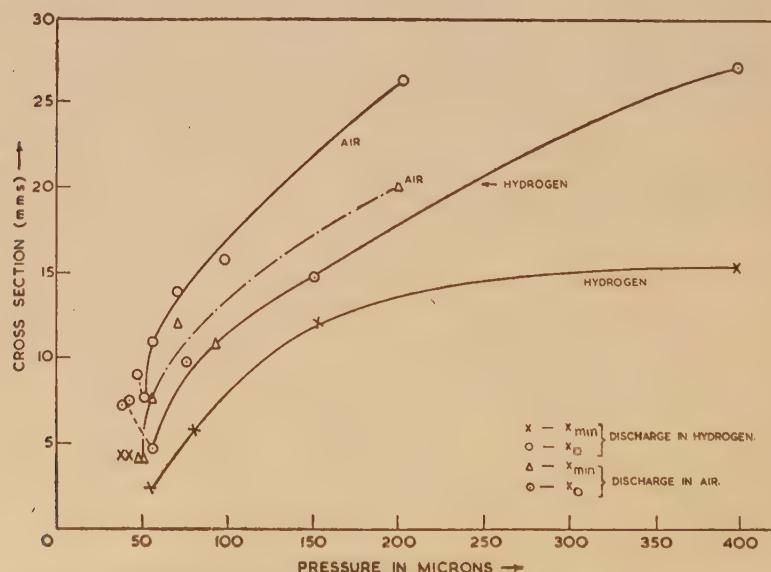


Fig. 2. Variation in the cross-section of discharge channel with pressure for discharge in air and hydrogen.

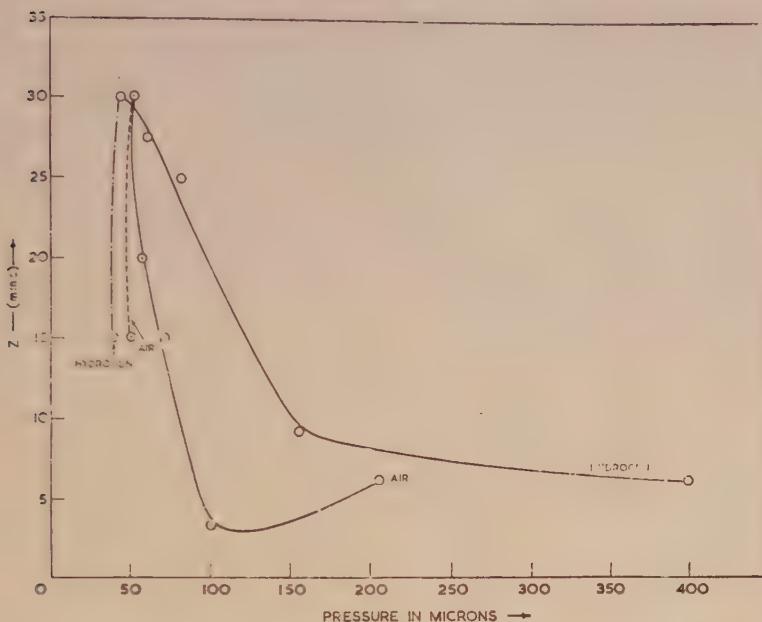


Fig. 3. Variation in the position of x_{min} with pressure for discharge in air and hydrogen.

(400–250 microns to 50 microns) the position of the minimum moves away from the cathode as the pressure is reduced. Its distance from the cathode reaches a maximum value at about this pressure; there are definite indications that it shows a sharp movement towards the cathode for pressures lower than this value.

The gradual constriction of the discharge channel from its origin at the beginning of the cathode dark space towards the cathode, could be explained in terms of the processes visualised in Kamke's theory (Kamke 1950). The increase in the cross-section in the neighbourhood of the cathode and its peculiar dependence on the pressure described above, however, may be taken to indicate the occurrence of a new process (like the photoelectric emission from the cathode) which is independent of the radial distribution of the positive ions coming towards the cathode. The positive ions and/or the fast neutral particles that enter this region have high velocities and therefore are not expected to be sensitive to changes in the nature and the distribution of the space-charge in this region; for although there is a net positive space-charge in the region of the cathode dark space, it is likely that the space-charge becomes electronic in the immediate vicinity of the cathode.

The variation of the H.W.R. with the pressure under the same conditions is shown in Fig. 4. The observations reveal that for the range of pressures (400–250 to 100–150 microns) there is a decrease of the H.W.R. with decreasing

pressure, a variation which is similar to the one observed for the x values for these pressures. The variation in the lower pressure range is, however, very peculiar; after reaching a minimum value for $p \sim 100-150$ microns the H.W.R.

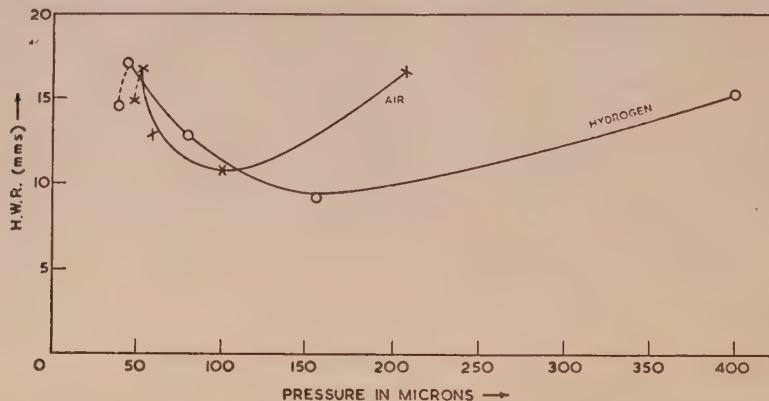


Fig. 4. Variation in the value of H.W.R. (at $Z = 0$) with pressure for discharge in air and hydrogen.

rises to a maximum for $p \sim 50$ microns (the same pressure for which x attains its minimum value) after which there are indications of a sharp fall. The physical significance of this observation does not seem to be clear at this stage.

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LIGHT SCATTERING IN CELLULOSE ACETATE SOLUTIONS*

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ABSTRACT. A detailed investigation of the light scattered by solutions of blank and dyed samples of cellulose acetate in acetone has been carried out. The method developed by Horn *et al.* has been employed for the estimation of molecular length L of the cellulose acetate molecules from the observed depolarisation factor ρ_v and the angular distribution of intensity. In a solution of dyed samples the dye molecules cause a shielding between the dyed molecules, thus producing a decrease in intermolecular interaction. Dyeing in general causes a straightening of the wave-like form of the cellulose acetate molecules thus producing an increase in molecular length. In this respect surface dyeing is less effective than either the interior dyeing or full penetration. The dispersion of depolarisation ρ_v and dissymmetry Z of the scattered light from these samples have also been discussed from considerations of intermolecular and intramolecular interactions.

INTRODUCTION

Light scattering studies on solutions of cellulose acetate in acetone were carried out for the first time by Doty and Kaufman (1945). A more extensive study on cellulose acetate was made by Stein and Doty (1946). They determined the particle size, shape and molecular weight of cellulose acetate in acetone and established that the smaller molecules were fully extended in solution i.e., the molecules were more or less rod-like, but the larger ones were built up in the form of gentle waves.

The present work on the scattering of light in cellulose acetate solutions was undertaken in order to study the effect of dyeing on cellulose acetate. Here the cellulose acetate molecules will be assumed to be rod-like after Stein and Doty (1946) because the theory of light scattering has been thoroughly dealt with for rod-shaped particles.

* Communicated by Prof. R. S. Krishnan.

2. PREPARATION OF SAMPLES

The cellulose acetate used here is a secondary cellulose acetate staple fibre soluble in acetone and only about 2.5 groups on an average are acetylated. For practical purposes this has been taken as blank cellulose acetate fibre.

The dyed samples of cellulose acetate were prepared in the following manner. The samples were deposited by double decomposition technique for PbCrO_4 , PbI_2 and Ag. The washed and boiled fibres were immersed in saturated lead acetate solution for a few hours, the excess liquid was squeezed out and then the fibre was immersed for a few hours in 5% $\text{K}_2\text{Cr}_2\text{O}_7$ for getting PbCrO_4 deposits. $\text{fibre} + \text{PbAc} \rightarrow \text{PbAc} + \text{fibre} + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{PbCrO}_4$ on fibre KAc etc. The fibre was immersed in polyiodide solution for PbI_2 deposits. For Ag deposits, the fibres were immersed in AgNO_3 solution for a few hours and the excess AgNO_3 solution was squeezed out. The fibres were then immersed in boiling 3% glucose solution, whereby reduction of Ag was completed. Fibres were all finally thoroughly washed, soaped and boiled in water, dried and combed out to remove loosely adhering particles.

Three types of dyeing were employed.

(a) *Fully penetrated* : This was accomplished by prolonged soaking of the fibres (1 week) in each of the solutions used.

(b) *Interior dyed* : These samples were obtained by stripping off from the fibre surface the deposits formed there using dilute acid for 15-25 seconds.

(c) *Surface dyed* : These were obtained by immersion in each of the solutions used for 15-30 minutes.

The dye deposits in the surface dyed samples are in the grooves of the surface only. Interior dyed fibres contain deposits only in the channels inside the fibre, while the fully penetrated dyed fibres are interior and surface dyed.

The eleven samples obtained are the following :—

1. Blank cellulose acetate
2. PbCrO_4 on cellulose acetate (fully penetrated)
3. " " " (surface dyed)
4. " " " (interior dyed)
5. PbI_2 " " (fully penetrated)
6. " " " (surface dyed)
7. " " " (interior dyed)
8. Ag " " (fully penetrated)
dev with H_2O_2
9. " " " (surface dyed)
10. Ag " " (fully penetrated)
dev with glucose
11. " " " (surface dyed)

10 mgs of each sample was carefully weighed and dissolved in 100 ml of double distilled analar acetone. This was taken as the parent solution. Its concentration was obviously 0.01 gm/ml. The lower concentrations of the samples were then prepared by diluting the parent solution adding known volumes of the solvent. In this manner for each sample, four different solutions with concentrations (0.01, 0.005, 0.0025 and 0.00125 gm/100 cc) were prepared.

These samples were prepared at the chemical laboratories of ATIRA and the physical measurements were carried out at the Physics Department of the Indian Institute of Science.

3. EXPERIMENTAL DETAILS

The measurements of the intensity of scattering were carried out with a photoelectric photometer constructed here. The optical arrangement is of the conventional type. A RCA 931-A photomultiplier tube served as a detector. A cathode follower amplifier was used to amplify the current from the PM. A balanced arrangement was employed to minimise the drift voltages. The amplified output was read on a microammeter or on a sensitive galvanometer when more accuracy was required. The readings obtained with this instrument were found to be quite reliable. This was checked by comparison with a Brice-Phoenix instrument.

Provision was made for interposing polaroids in the incident and scattered sides for getting vertically and horizontally polarised components. The sensitivities of the photomultiplier set up for vertically and horizontally polarised light were measured and the differences were found to be usually less than two per cent. Necessary corrections were made in the readings taken with the instrument while working with cellulose acetate solution.

The sample to be studied was kept in a cylindrical glass vessel which was provided with flattened openings for entrance and exit of the incident beam. Measurements of the angular distribution of the intensities of the three components V_v , V_h and H_h of the scattered light were carried out for the following values of the scattering angle θ ; 45° , 55° , 65° , 75° , 90° , 105° , 115° and 125° from the forward direction. For each sample the angular distribution of the intensity of scattered light were measured for three different wavelengths, namely, 4358 \AA , 5461 \AA , 5790 \AA and for four different concentrations. All the readings were converted to the same arbitrary unit. These values were corrected for effective volume by multiplying them by the corresponding value of $\sin \theta$.

4. RESULTS

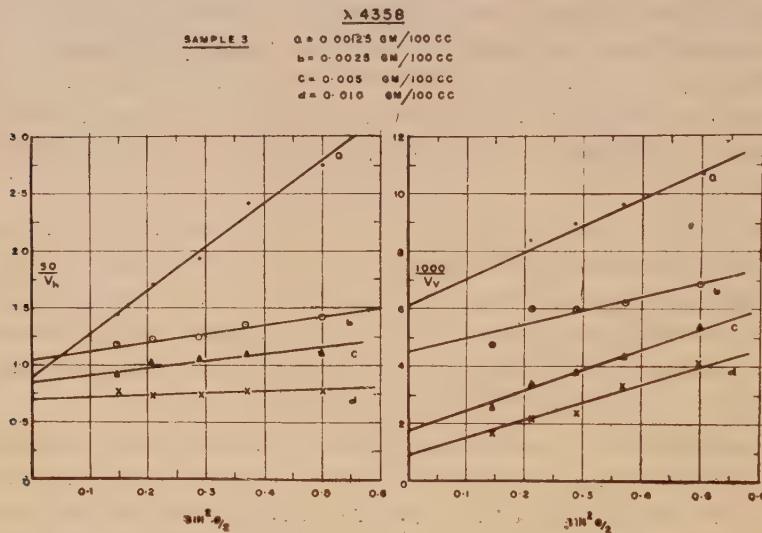
Table I gives the corrected values of intensity of scattering for various angles for the three components for one typical case, namely, PbCrO_4 on cellulose acetate (interior dyed) of concentration 0.005 gm/100 cc at 5461 \AA .

TABLE I

Intensity values

θ	45°	55°	65°	75°	90°	105°	115°	125°
V_h	64	64	60	58	54	61	63	64
H_h	699	400	336	266	192	151	152	147
V_v	847	540	446	365	276	191	152	152

The method of determining anisotropy was similar to those employed by Horn *et al.*, (1951) and Horn (1955). The values of V_h and V_v for zero angle of scattering were extra-polated from the curves drawn with $1/V_h$ and $1/V_v$ as a function of $\sin^2 \theta/2$. Curves obtained in a typical case are shown in Fig. 1.

Fig. 1. Variation of $1/V_h$ and $1/V_v$ with $\sin^2 \theta/2$.

These curves were more or less linear. From the limiting values of V_h and V_v the corresponding values of ρ_v at $\theta = 0^\circ$ were calculated. The procedure was adopted for each sample. Curves were drawn with concentration as abscissa and ρ_v at $\theta = 0^\circ$ as ordinate and the limiting value ρ_v at zero concentration and zero angle designated as ρ_v^0 was estimated. Curves obtained in a typical case are shown in Fig. 2. The anisotropy factor δ was determined by using the formula $\rho_v^0 = 3\delta^2/(5+4\delta^2)$. The sign of anisotropy of the molecule was determined from the behaviour of the curve H_h versus $\sin \theta/2$ (Horn, 1955). From a study of the experimental H_h versus $\sin \theta/2$ curves here in conjunctions with the arguments of Horn, indicated that the anisotropy had a negative sign.

Knowing the value of anisotropy δ , the theoretical values of V_v were calculated using the approximate formula of V_v given by Horn *et al.* (1951). Theore-

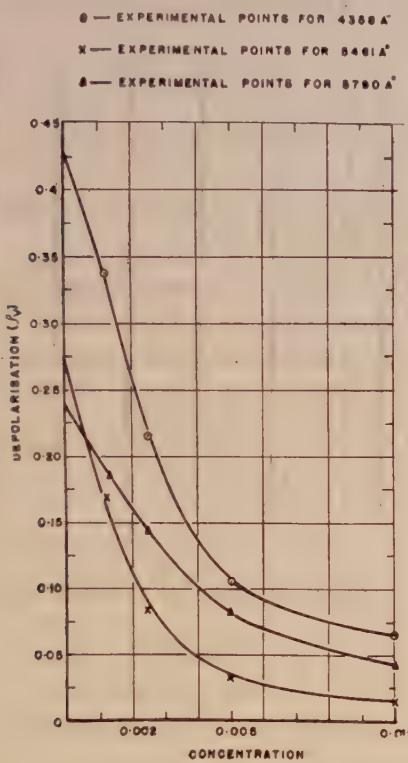


Fig. 2. Variation of ρ_v with concentration.

tical graphs of V_v against $\sin \theta/2$ for various values of L/λ' and different values of δ were drawn.

Since the theory developed by Horn *et al.* is true only for low concentrations, all the corrected values of V_v were extrapolated to zero concentration for various angles of scattering. A graph was drawn showing the experimental V_v value at zero concentration as a function of $\sin \theta/2$. The curve thus obtained was matched for coincidence with the proper set of theoretical curves mentioned above for obtaining the corresponding value of L/λ' . The typical curves are shown for one sample in Fig. 3. Knowing L/λ' , the length of the rod-shaped cellulose acetate particles, L , was calculated. The procedure was repeated for all the three wavelengths and the mean value of L for each sample was determined. The deviations in the value of L for each wavelength was less than 50 A.U. The mean values of L for all samples are given in Table II.

The depolarisation ρ_v at $\theta = 90^\circ$ was determined by taking the ratio of the intensity components V_h and H_v at 90° and the dissymmetry ratios $I_{55^\circ}/I_{135^\circ}$ by

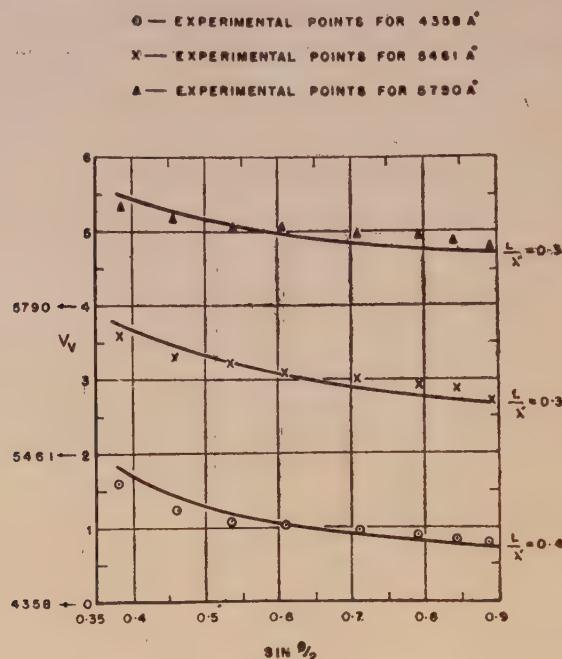
Fig. 3. Variation of V_v with $\sin \theta/2$.

TABLE II
Particle length

No.	Samples	Length A.U.
1.	Blank cellulose acetate	560
2.	PbCrO ₄ (F. Penetrated)	430
3.	PbCrO ₄ (S. Dyed)	960
4.	PbCrO ₄ (I. Dyed)	1280
5.	PbI ₂ (F. Penetrated)	980
6.	PbI ₂ (S. Dyed)	640
7.	PbI ₂ (I. Dyed)	1040
8.	Ag (F. Penetrated) dev. H ₂ O ₂	1165
9.	Ag (S. Dyed)	900
10.	Ag (F. Penetrated) dev. glucose	1200
11.	Ag (S. Dyed)	1160

taking the total intensity of the components i.e., ($V_v + 2V_h + H_h$) for each angle. Typical results obtained with eleven samples for one concentration, namely 0.005 gm/100 cc., are given in Table III.

TABLE III
 Depolarisation $\rho_v \%$, dissymmetry Z

Samples No.	Dimensions AU	4358 Å	5461 Å	5790 Å	4358 Å	5461 Å	5790 Å	Total intensity at 90° for 5461 Å zero concn.
1	560	9.8	5.5	7.0	4.08	5.17	3.59	190
2	430	6.5	6.1	6.4	3.90	4.94	3.45	90
3	960	25.0	21.6	24.4	2.54	3.18	2.35	155
4	1280	24.0	19.6	24.0	1.83	2.42	1.60	180
5	980	33.3	30.6	26.4	1.96	2.46	1.80	185
6	640	8.7	9.5	8.5	2.80	3.69	2.80	120
7	1040	25.0	23.0	27.0	2.69	3.01	2.43	130
8	1165	29.0	30.3	29.0	2.15	2.80	2.09	150
9	900	11.6	9.3	11.2	2.69	3.37	2.56	130
10	1200	28.9	27.3	26.0	1.93	2.76	1.95	190
11	1160	34.7	28.7	31.2	2.13	2.90	2.08	170

5. DISCUSSION

It is well known that the dissymmetry of scattering arises from interferences due to interaction of waves scattered by different parts of the molecule (intra-molecular) and also due to the interaction between the waves originating from different molecules (intermolecular).

The dependence of dissymmetry on concentration assuming the hard sphere model has been given in an approximate form by Oster (1949) and Doty *et al.* (1951). This can be written as $Z = Z_0 \left(1 - \frac{Kc}{\lambda^2}\right)$ where Z_0 is the dissymmetry at zero concentration. This equation can be extended to the case of rods.

From the above equation it is evident that the presence of intermolecular effect is to increase the dissymmetry with wavelength and is proportional to $\left(1 - \frac{K}{\lambda^2}\right)$ Mommaerts (1951, 1957), Oster (1948, 1949). The presence of intra-molecular effect is to decrease the dissymmetry as the wavelength increases and is proportional to $1/\lambda$ (Horn, *et al.*, 1951). At finite concentration these two effects will contribute to the total dissymmetry and hence the dispersion of dissymmetry may not be linear. This has been observed experimentally.

It is seen from the figure of dissymmetry against L/λ' for various values of δ (Horn 1955) that for one value of Z , δ increases as L/λ' increases, i.e., δ in-

creases as λ decreases at infinite dilution. But $\rho_v = 3\delta^2/5 + 4\delta^2$. Therefore ρ_v increases as λ decreases. From the same figure we also note that for any one value of L/λ dissymmetry increases as ρ_v decreases. Thus the variation of depolarisation factor ρ_v with wavelength is opposite to the variation with wavelength of dissymmetry.

In Table II are given the estimated values of the molecular length of eleven cellulose acetate samples. It is seen that the lengths of the dyed samples are in general greater than that of blank cellulose acetate sample. This increase in length of the dyed samples can be explained as a straightening of wavelike form of cellulose acetate chain as the dye penetrates into its pores. The lengths of the cellulose acetate molecules in fully penetrated sample and interior dyed sample are nearly the same but greater than that in surface dyed samples. In the case of sample 2, vide Table II, the micellar length comes out to be smaller than the corresponding values of the other samples. The depolarisation factor ρ_v is also the lowest for this sample. In the process of preparing the fully penetrated dyed sample, the micelles appear to have broken into smaller sizes.

ACKNOWLEDGMENTS

The authors wish to express their sincere thanks to Professor R. S. Krishnan for guidance and encouragement. Thanks are also due to Dr. P. S. Narayanan and Mr. S. Subramanian for valuable discussions.

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A COMPARATIVE STUDY OF SINGLET → TRIPLET ABSORPTION IN SOME HALOGENATED TOLUENES IN THE VAPOUR AND LIQUID STATES*

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ABSTRACT. The absorption spectra in the near ultraviolet region due to singlet → triplet transition in the vapours of *o*-chlorotoluene, *p*-chlorotoluene, *m*-bromotoluene and *p*-bromotoluene at 24°C have been investigated using a path length of 18.9 metres at the respective saturation vapour pressures and these spectra have been compared with those for the equivalent path lengths of the liquids. It has been observed that the absorption due to singlet → triplet transition is of continuous nature and the long wavelength limit of maximum absorption in the liquid state is found to be at about 29000 cm⁻¹ for all the compounds, but in the case of the vapours the limit is shifted towards higher frequencies, the shift being smaller for the para compounds than for the ortho or meta compounds. It has been concluded that singlet → triplet transition is enhanced by the influence of heavy atoms of the surrounding molecules in the liquid state.

INTRODUCTION

Kasha (1952) reported that the very weak singlet → triplet absorption bands of α -chloronaphthalene is strengthened considerably in solution in ethyliodide, and he attributed this to an intermolecular spin-orbit perturbation due to the heavy iodine atom (Z-effect). Later, McClure *et al.* (1954) also observed the Z-effect in singlet → triplet absorption bands of halogen substituted benzenes and naphthalenes and put forward a simple theory to explain it. The dependence of intensity of continuous absorption due to singlet → triplet transition on the atomic number of the substituent atoms in the case of some halogenated toluenes in the liquid state was also studied by Roy (1960).

It was first shown by Evans (1956) that the discrete absorption bands around 3300 Å observed by previous workers in the spectra due to long absorption path of liquid benzene disappear when the dissolved atmospheric oxygen is removed from the liquid. He next studied (Evans, 1957a) the absorption spectra of solutions of benzene, fluorobenzene, diphenyl, styrene and fluorene in chloroform

*Communicated by Professor S. C. Sircar.

saturated with oxygen gas at high pressures and observed some discrete bands due to singlet→triplet absorption in most of the cases. He further observed that in the case of solution of α -bromonaphthalene there was only continuous absorption in the region 4000 Å—5000 Å, but when the solution was saturated with oxygen gas at a pressure of 76 atmospheres sharp bands appeared in this region without appreciable rise in the absorption coefficient. On the other hand, he observed that when a 0.9M solution of naphthalene in chloroform was saturated with oxygen gas at different pressures up to 100 atmospheres, the absorption coefficient increased proportionately with the increase in the pressure of the gas.

Robertson and Reynolds (1958) carried out an interesting experiment to prove the correctness of the theory of probability of singlet→triplet transition put forward by McClure (1949, 1952) and by Mizushima and Koide (1952). Kasha (1952) had suggested that the probability of singlet→triplet transition is enhanced when the molecules are surrounded by heavy atoms owing to the perturbation of the spin-orbital coupling by the heavy atoms. Since the spin-orbital coupling operator depends on the inverse third power of the distance between the π -electron and the heavy atom, Kasha (1952) suggested that hydrostatic pressure would increase the perturbation. Robertson and Reynolds (1958) subjected a mixture of α -chloronaphthalene and ethyliodide to pressures ranging from 1 to 3644 atmospheres and observed that there was a two-fold increase in the singlet→triplet absorption with the increase of pressure mentioned above. In the case of pure α -chloronaphthalene, however, the singlet→triplet absorption was much weaker and no such pressure effect was observed.

The perturbation of the spin-orbital coupling by the magnetic field of surrounding paramagnetic molecules in the gaseous state was first observed by Evans (1957b). He introduced in the absorption cell containing vapours of either benzene or fluorobenzene at a pressure of 70 mm of Hg oxygen gas at pressures up to 130 atmospheres and observed intense absorption bands in the region 3000 Å—3400 Å. The influence of neighbouring molecules of the same kind on such singlet→triplet absorption was, however, not known and it was recently investigated by Sirkar and Roy (1960) using long absorbing paths of the vapour. It was observed by them that benzene vapour at a pressure of 120 mm and with path length 18.90 metres shows only very feeble continuous absorption in the region 3000 Å—3400 Å and an equivalent path length of liquid benzene shows very slightly stronger absorption in this region. In the case of *o*-bromotoluene vapour with similar path length, however, the continuous absorption in the region 3400 Å—3600 Å was observed to be much stronger and it increased considerably when an equivalent path length of the liquid was used. These results show that the spin-orbital coupling of the π -electron is perturbed by heavy atoms in surrounding molecules of the same kind. In order to find out whether such a general conclusion can be drawn from these results, the investigations have been extended

to a few other substituted benzene compounds and the results have been discussed in the present paper.

EXPERIMENTAL

The substances selected for studying the absorption spectra due to singlet→triplet transition in the present investigation are orthochlorotoluene, parachlorotoluene, matabromotoluene and parabromotoluene. Chemically pure samples of *o*-chlorotoluene and *p*-chlorotoluene obtained from British Drug House, England, *p*-bromotoluene obtained from Fisher Scientific Company, U.S.A. and *m*-bromotoluene from City Chemical Corporation, New York, U.S.A. were distilled several times under reduced pressure before being used in the investigation.

The experimental arrangement was the same as that employed in an earlier investigation (Sirkar and Roy, 1960). The absorption spectra of the substances in the vapour state were photographed first by filling up the absorption cell, 18.90 metres long, with the vapours of the compounds at the saturation pressures at about 24°C. The pressure was measured carefully with a differential manometer and the short empty cell for the liquid was also placed in the path of light in order to take into account the loss of incident light during its passage through this empty cell. The pressure was found to be about 55 mm for the bromotoluenes and about 50 mm for the chlorotoluenes. After photographing the absorption spectrum of the vapour of each of the compounds the long vapour cell was evacuated and the short cell of length 7 mm for the bromo compounds and 6.5 mm for the chloro-compounds was filled with the distilled liquid and the absorption spectrum of the liquid was photographed on the same film with the same time of exposure and under identical conditions. In order to test the genuineness of the absorption observed in case of the substances in the vapour state with a path length of 18.90 metres, the absorption spectra were also studied for shorter path lengths. Using a path length of 9.45 metres, the absorption spectrum of *p*-bromotoluene in the vapour state was, therefore, photographed and compared with the spectrum for a path length of 3.5 mm of the liquid. A Hilger medium quartz spectrograph and Agfa Isopan films were used to photograph the spectra. The time of exposure was about 10 hours in every case. Iron arc spectrum was photographed in each spectrogram as comparison. Microphotometric records of the spectrograms were obtained with a self-recording microphotometer supplied by Kipp and Zonen. The wavelengths in the continuous absorption spectra were measured by drawing a sharp line on the film in the position of a known iron line in the adjacent iron arc spectrum and comparing the microphotometric records of the iron arc and absorption spectra.

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra due to pure meta-bromotoluene and parabromotoluene in the liquid and vapour states are repro-

duced in Figs. 1(a)—1(d), respectively, and the absorption spectra due to pure orthochlorotoluene and parachlorotoluene in the liquid and vapour states are reproduced in Figs. 2(a)—2(d), respectively. Figs. 3(b) and 3(a) show the spectra due to path lengths of 9.45 metres of *p*-bromotoluene in the vapour state, and 3.5 mm of the liquid respectively. The reference line in the records has the wavelength 4051 Å.

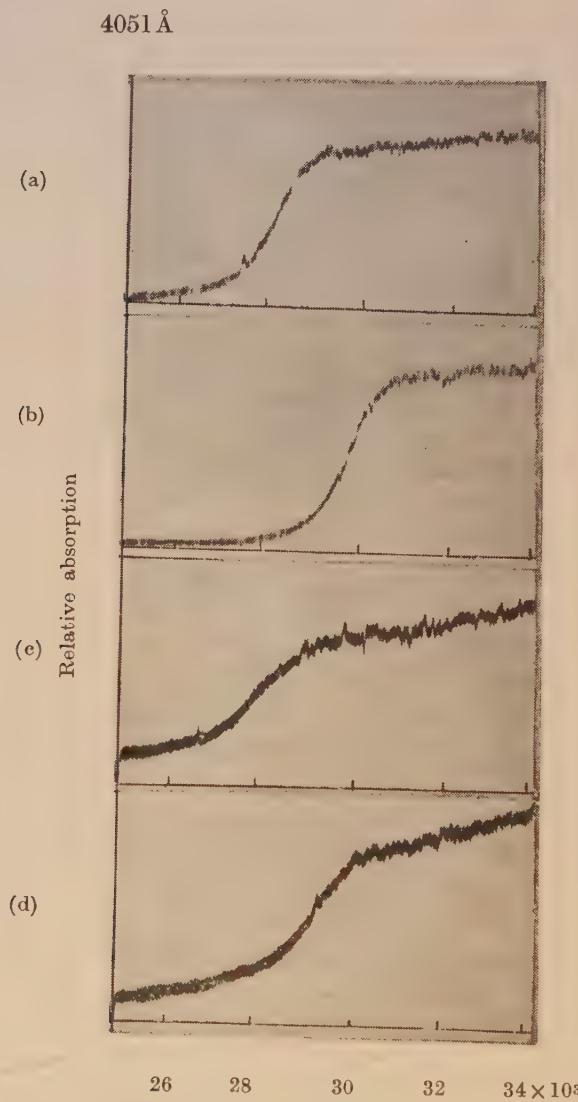


Fig. 1. (a) *m*-Bromotoluene (liquid);
 (b) " (vapour)
 (c) *p*-Bromotoluene (liquid)
 (d) " (vapour)

The microphotometric records of the absorption spectra reproduced in Figs. 1 and 2 show that in the cases of all the four compounds the absorption spectrum due to the liquid is displaced towards red with respect to that due to the vapour phase. This shift is however, different for the different compounds.

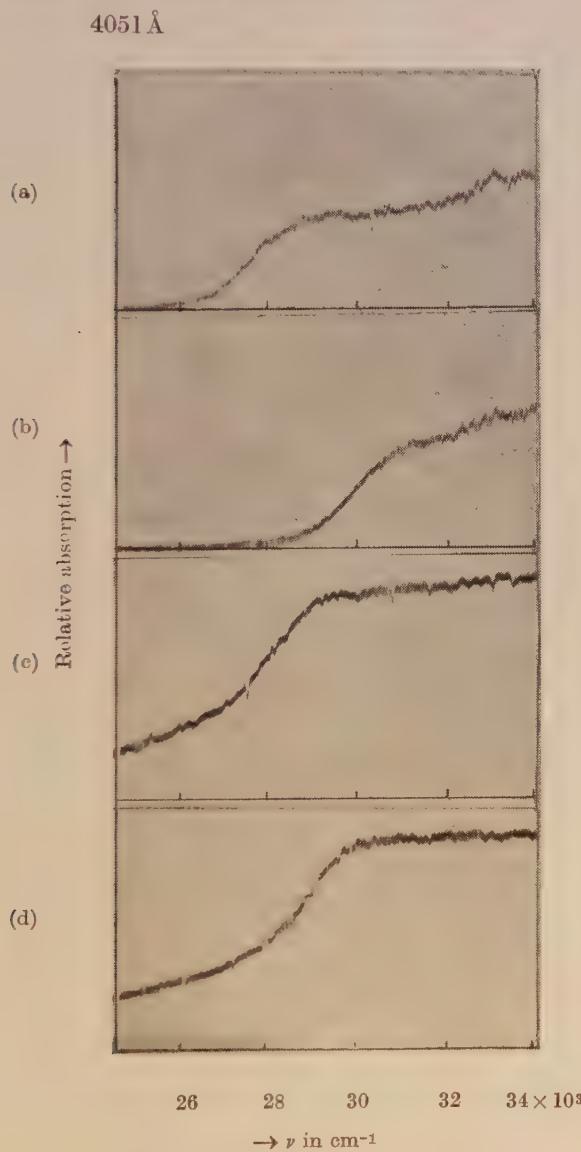


Fig. 2. (a) *o*-Chlorotoluene (liquid)

(b) " (vapour)

(c) *p*-Chlorotoluene (liquid)

(d) " (vapour)

A comparison of the curves in Fig. 1 shows that the spectrum due to the parachlorotoluene in the vapour state is shifted towards red by about 1000 cm^{-1} with respect to that due to the ortho compound in the vapour state. Similarly, Fig. 2, shows that the spectrum due to *p*-bromotoluene in the vapour state is shifted towards red by about 500 cm^{-1} with respect to that due to the meta compound. When the vapours are liquefied there is further shift of the spectrum towards red, but although in the case of *o*-chlorotoluene the position of maximum absorption on the long wavelength side shifts from 31000 cm^{-1} to 29000 cm^{-1} with the liquefaction of the vapour, such shift is from 29600 cm^{-1} to 29000 cm^{-1} in the case of *p*-chlorotoluene. In the case of *p*-bromotoluene, on the other hand, such shift is from 30000 cm^{-1} to 29000 cm^{-1} and in the case of *m*-bromotoluene the shift is a little more, being from 30500 cm^{-1} to 29000 cm^{-1} . As the $0,0$ band due to singlet \rightarrow singlet transition occurs in the neighbourhood of 36000 cm^{-1} (Roy, 1956) in all these cases, the absorption in the region of 30000 cm^{-1} cannot

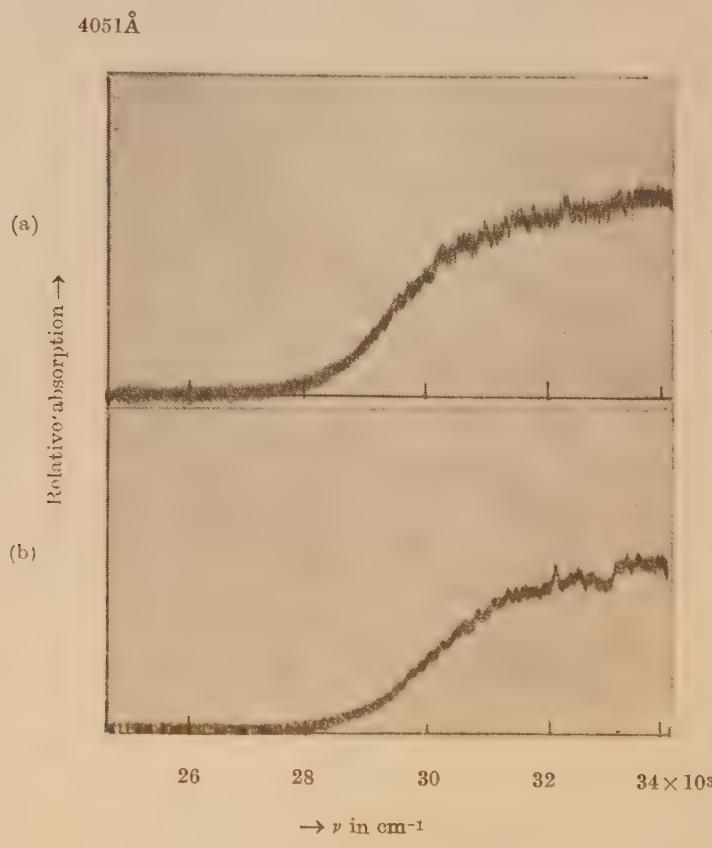


Fig. 3. (a) *p*-Bromotoluene (liquid)

(b) " (vapour)

be due to an extension of the singlet→singlet absorption towards longer wavelengths, and therefore, it is due to singlet→triplet transition. A comparison of Fig. 1(d) with Fig. 3(b), further shows that when the path length of the vapour is halved, the absorption in the region from 30000 cm^{-1} to 31000 cm^{-1} diminishes considerably. This shows the genuineness of the absorption due to the longer path of the vapour.

It is evident from the above results that probability of such transition is enhanced much more in the case of ortho or meta halogen substituted toluenes than in the case of the para compounds, when the vapours are liquefied. It is to be pointed out further, that the wavelength limit of maximum absorption in the liquid state is almost at the same position (about 29000 cm^{-1}) in all the four cases. It is evident from these results that the enhancement of singlet→triplet absorption with the liquefaction of the vapour is due to the influence of the substituent halogen atoms in the surrounding molecules in the liquid state, because in the case of benzene such enhancement is extremely small (Sirkar and Roy, 1960) The difference observed in the case of the para compound and that in the case of ortho or meta compound can be explained on the hypothesis that as in the case of the para compound the halogen atom is far away from the CH_3 group it acts as a better shield against the interaction between the π -electrons of the ring and the halogen atom of the neighbouring molecule than in the case of the ortho or meta compound. In the ortho compound, the π -electrons in consecutive four carbon atoms being exposed to the influence of the halogen atom in the neighbouring molecule, there may be greater chance of the perturbation of the spin-orbital coupling than in the case of the para compound.

It can be seen from the curves in Figs. 1 and 2 that the absorption spectrum due to singlet→triplet transition is of continuous nature. As mentioned earlier, some previous workers observed discrete bands due to singlet→triplet transition induced by the influence of paramagnetic molecules on the π -electrons. It is highly probable that some preferentially orientated magnetic field due to the paramagnetic molecules produces such quantised new levels of the π -electrons while in the field of surrounding heavy atoms, such field has only random orientation giving rise to very broad perturbed levels.

ACKNOWLEDGMENT

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INFRARED SPECTRA OF *O*-BROMOPHENOL IN THE LIQUID STATE AND IN SOLUTIONS IN DIFFERENT SOLVENTS*

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ABSTRACT. The infrared spectra of *o*-bromophenol in the liquid state and in solutions in carbon tetrachloride, cyclohexane and chloroform in the 3200-3700 cm^{-1} region have been studied with a Perkin-Elmer Model 21 spectrophotometer. As regards the OH band, the pure liquid exhibits a broad absorption band at about 3460 cm^{-1} while sharp peaks at 3522, 3522 and 3490 cm^{-1} are exhibited by 3% solutions of the compound in carbon tetrachloride, cyclohexane and chloroform respectively. In the case of 12% solutions in carbon tetrachloride and cyclohexane, sharp peaks at 3474 and 3484 cm^{-1} are observed. In each of these two cases there is also an inflexion at about 3540 cm^{-1} .

It has been concluded that in the liquid state most of the molecules are present as dimers as suggested by Pauling and in the case of the dilute solutions the majority of the molecules are single. It has been pointed out that an idea of relative abundance of associated molecules and single molecules can be found from a comparison of the areas of the absorption peaks due to these two types of molecules present in concentrated solutions.

INTRODUCTION

In explaining the infrared spectrum of *o*-chlorophenol, Pauling (1945) pointed out that the liquid may contain double molecules formed through O-H...O intermolecular bond, while the OH group and chlorine atom of the same molecule may be linked in the *cis*-position. In a recent investigation on the infrared spectra of dilute solutions of *o*-chlorophenol in carbon tetrachloride and cyclohexane (Sirkar *et al.*, 1958) it was observed that the intermolecular hydrogen bond in associated molecules breaks up in dilute solutions. Davies (1940) studied the infrared spectrum of *o*-bromophenol in dilute solutions in carbon tetrachloride and observed a band at 3520 cm^{-1} and a weaker one at 3595 cm^{-1} , which were assigned by him to the O-H frequencies in the case of the OH group respectively in *cis*- and *trans*-position with respect to the bromine atom in the same molecule. Similar investigations in the first harmonic region were also reported by Wulf *et al.* (1936). They, however, did not report any data for the pure liquid. In the

*Communicated by Professor S. C. Sirkar.

present work it was, therefore, intended to study the nature of hydrogen bonding in *o*-bromophenol in the liquid state and the influence of environment on the population of such associated molecules, and the infrared spectra of *o*-bromophenol in the liquid state and in solutions of different concentrations in carbon tetrachloride, cyclohexane and chloroform, have been studied. The results have been discussed in the present paper.

EXPERIMENTAL

Chemically pure *o*-bromophenol purchased from E. Merck was fractionated and the proper fraction was collected and redistilled under reduced pressure. Carbon tetrachloride, cyclohexane and chloroform used as solvents were also of chemically pure quality and were also distilled under reduced pressure before use.

The infrared spectra were recorded with a double beam Perkin-Elmer Model 21 spectrophotometer with rocksalt optics. The slit was adjusted at 927. The instrument was placed in an airconditioned room maintained at a temperature of 26°C.

The strengths of solutions used were 3% and 12% for solution in carbon tetrachloride and cyclohexane and 3% for solution in chloroform. The thickness of the cell was 0.1 mm in the case of dilute solutions and 0.025 mm in the case of the concentrated solutions. The spectrum of the pure liquid was recorded using a thin film of the liquid pressed between two rocksalt plates. In studying the spectra of the solutions, the bands of the solvents were eliminated by using an equivalent compensation cell containing the solvents in the reference beam.

RESULTS AND DISCUSSION

The absorption curves due to *o*-bromophenol and its solutions in carbon tetrachloride, cyclohexane and chloroform are reproduced in Figs. 1 and 2. In the case of the pure liquid broad absorption extending from 3550 cm^{-1} to 3200 cm^{-1} is observed which suggests that the absorption curve is produced by superposition of more than one broad bands. The maximum of absorption is at about 3460 cm^{-1} which is broadened towards lower frequencies with a gradual fall in intensity. In 3% solution in carbon tetrachloride and cyclohexane, however, the intense broad band at 3460 cm^{-1} is totally absent and only a sharp peak at 3522 cm^{-1} is observed. Davies (1940) observed a band at 3520 cm^{-1} and a very much weaker band at 3595 cm^{-1} in the spectrum of .09M solution of *o*-bromophenol in carbon tetrachloride. He attributed the first band to the O-H vibration in the OH group in the *cis*-position with respect to bromine atom and the second one to the O-H group in the *trans*-position. On comparing these results, it appears that the intense broad peak at 3460 cm^{-1} in the pure liquid may represent the O-H vibration in the dimeric molecules present in the liquid, the

hydrogen atom of the OH group of a molecule being attached to the oxygen atom in a neighbouring molecule (Pauling, 1945).

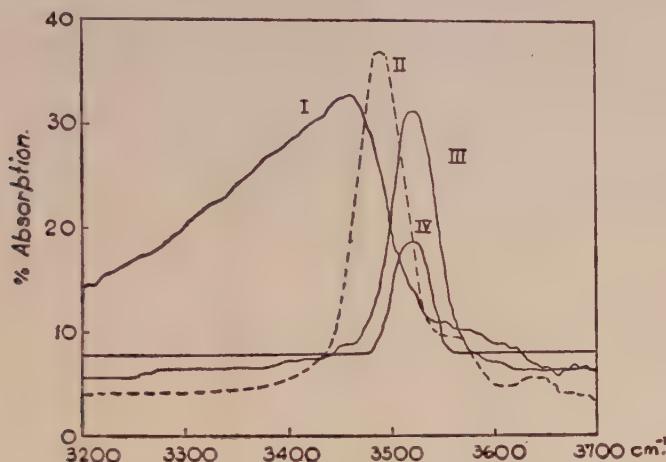


Fig. 1. Infrared absorption spectra of *o*-bromophenol
 Curve I. Pure liquid
 Curve II. 3% solution in chloroform
 Curve III. 3% solution in carbon tetrachloride
 Curve IV. 3% " " cyclohexane

When the molecules are dispersed in 3% solutions in carbon tetrachloride and cyclohexane, the intermolecular O-H...O bond is broken and the observed frequency at 3522 cm^{-1} represents the O-H stretching oscillation in the OH group in the single molecule. As pointed out in a previous paper (Sirkar *et al.*, 1958) this frequency may not belong to *cis*-configuration. The peak due to solution in CCl_4 is, however, much larger than that due to the solution in cyclohexane. This shows the influence of the environment on the strength of absorption. The weak OH stretching band assigned to *trans*-molecules reported by Davies has, however, not been observed in the present investigation. In 3% solution of *o*-bromophenol in the polar solvent chloroform, the OH vibrational frequency is only at 3490 cm^{-1} , which may indicate an influence of the field of the polar solvent molecules on this frequency of the dispersed molecules of *o*-bromophenol.

When the concentration of *o*-bromophenol in carbon tetrachloride and cyclohexane is increased to 12%, sharp peaks at 3474 and 3484 cm^{-1} respectively are observed. In this case the strength of absorption is also relatively higher than at 3522 cm^{-1} in the case of the 3% solution with equivalent path length. This peak is accompanied in each case by a weak inflexion at about 3540 cm^{-1} . Thus the concentrated solutions in both the solvents seem to contain large number of dimeric molecules and a few single molecules and the two frequencies due to

each of these 12% solutions probably represent OH stretching oscillations in intermolecular OH...O bonded group and in the OH group in the *trans*-position in the single molecule as pointed out by Sirkar *et al.* (1958).

It is interesting to note that the results discussed above give definite indication of the predominance of dimeric molecules in the pure liquid state of

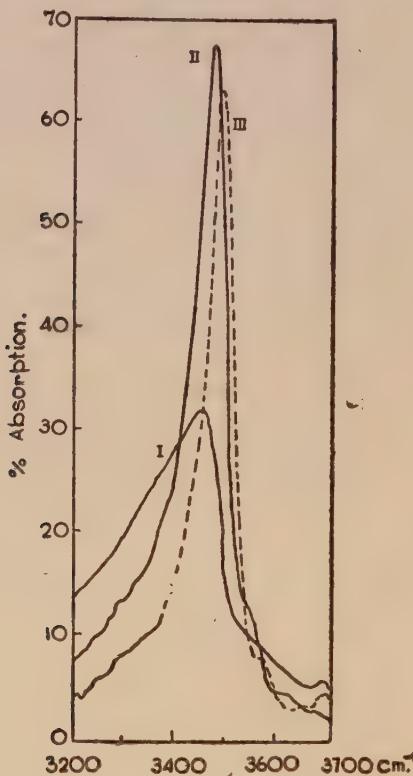


Fig. 2. Infrared absorption spectra of *o*-bromophenol
 Curve I. Pure liquid
 Curve II. 12% solution in carbon tetrachloride
 Curve III. 12% solution in cyclohexane

o-bromophenol and also give an idea about the relative abundance of dimeric molecules over the *trans*-type single molecules in the case of solutions of concentration above 10%. In fact, a quantitative estimation of the relative population of O-H...O bonded double molecules with OH group in *cis*-configuration with respect to that of the single molecules can be made from the ratio of the areas of the peaks at 3474 cm^{-1} and 3540 cm^{-1} respectively observed in the case of concentrated solutions if the change in the strength of absorption per molecule with the change from the *trans* to the *cis* position of the OH group is first determined.

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ON THE ABSORPTION OF 3.18-CM MICROWAVES IN SOME ALIPHATIC ALCOHOLS AND THEIR SOLUTIONS*

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ABSTRACT. The dependence on temperature of absorption of microwaves of wavelength 3.18 cm in *n*-propyl, *n*-butyl, isopropyl-, isobutyl-, *n*-octyl- and *n*-heptyl alcohol and in their solutions in CCl_4 and heptane at different concentrations have been studied by simple optical method.

It is observed that in the case of lower alcohols absorption increases with the increase of temperature without showing any definite maximum in the curve, while the higher alcohols and the solutions of all the six alcohols show absorption maxima at temperatures depending on their viscosities.

From a comparison of different results it has been concluded that most of the molecules in the lower alcohols in the pure state are in the form of dimers which break up in the solutions into single molecules. In the case of higher alcohols the molecules being large, some of the molecules do not form such dimers and remain as single molecules.

Applying Debye's theory the radius of the rotor has been calculated, and the value has been found to be near about 1.96 Å in all the cases. The rotor has been indentified with the OH group.

INTRODUCTION

The anomalous dielectric dispersion in alcohols in the region of radio-waves of wave-lengths ranging from decimetre to metre region was studied by Mizushima (1927). He found that some aliphatic alcohols show absorption in the metre region and the region of such anomalous dispersion shifts towards longer wave-lengths as the length of the molecule increases. With a particular frequency he observed (Mizushima, 1929) that the temperature at which the maximum absorption occurs becomes higher for higher alcohols. He concluded that the theory proposed by Debye (1913) correlating time of relaxation with the dielectric constant at any frequency was verified by these results and that the whole molecule was the rotor in these cases. Later, Ghosh (1954, 1955) studied the absorption of 3.18cm microwaves in some aromatic liquids with the molecules having OH group as a

*Communicated by Prof. S. C. Sirkar

substituent and by varying the temperature of the liquids he observed maximum absorption at a particular temperature in each case. From the values of the time of relaxation and the viscosity of the liquids at those temperatures he calculated the radius of the rotor and found it to be of the order of 1.5 Å. He concluded that the rotor was the OH group and not the whole molecule in these cases.

Recently, Imanov and Abbasov (1957) used microwaves of wave-lengths ranging from 10 cm to 180 cm to measure the dielectric loss in several normal and iso-alcohols in this region. They observed maximum loss at particular wave-lengths in the region from 18 cm to 60 cms in five alcohols, but no such maxima were observed in methyl and ethyl alcohol in the whole wave-length range 12 cm—180 cm. They did not identify the rotor in the above cases.

It would be interesting, however, to find out whether in these pure aliphatic alcohols in the liquid state the OH group has any freedom of rotation and whether the influence of solvents affects such freedom. With this object in view the absorption of 3.18 cm microwaves in a few aliphatic alcohols in the liquid state and also in solution in suitable solvents has been investigated.

EXPERIMENTAL

The experimental arrangements and procedure adopted in the present investigations were the same as those used previously (Bhattacharyya 1958). The liquids used were *n*-propyl-, *n*-butyl-, isopropyl-, isobutyl-, *n*-heptyl-, and *n*-octyl alcohol. In order to make the alcohols free from water the lower alcohols were mixed with dehydrated magnesium sulphate and were kept in this condition for two days. After filtration they were treated with fresh quick-lime and subjected to fractional distillation. The two higher alcohols were distilled in vacuum after proper dehydration. The absorption was studied in the pure liquids as well as in their solutions of different concentrations in CCl_4 and heptane in the range of temperature from 28°C to 140°C. The graphs showing the relation between temperature and the attenuation coefficients of different liquids were drawn. The values of static dielectric constant, refractive indices and coefficients of viscosity for the pure liquids were obtained from the standard tables. These data for the solutions were determined experimentally. With the help of Debye's theory and using these data, the radius of rotor was calculated in each case.

RESULTS AND DISCUSSIONS

Fig. 1 shows the temperature-dependence of the attenuation coefficients of pure alcohols. The lower alcohols like *n*-butyl-, *n*-propyl-, isobutyl- and isopropyl alcohol do not show any absorption maxima. The absorption in these cases increases rapidly with the increase of the temperature. Similar results were also obtained in the case of pure ethylene chlorhydrin (Bhattacharyya, 1959). The higher alcohols, however, show definite absorption maxima. Octyl alcohol

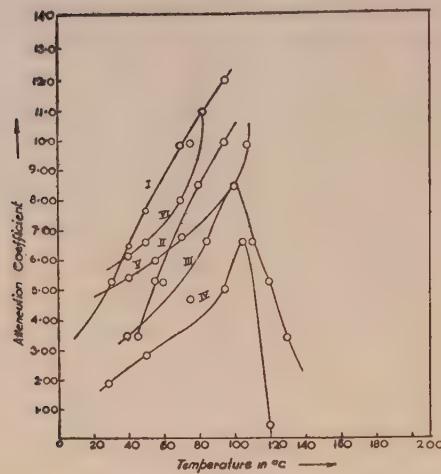


Fig. 1. Temperature dependence of the attenuation coefficient for pure alcohols.

- I—*n*-Propyl alcohol.
- II—*n*-Butyl alcohol.
- III—*n*-Heptyl alcohol.
- IV—*n*-Octyl alcohol.
- V—iso-Butyl alcohol.
- VI—iso-Propyl alcohol.

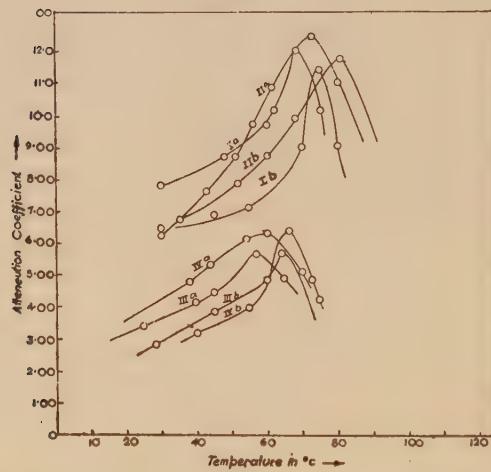


Fig. 2. Temperature dependence of the attenuation coefficient of the solutions of *n*-alcohols in CCl_4 .

Ia—20% solution of heptyl alcohol in CCl_4 .
 Ib—30% " " " " " "
 IIa—20% solution of octyl alcohol in CCl_4 .
 IIb—30% " " " " " "
 IIIa—30% solution of propyl alcohol in CCl_4 .
 IIIb—50% solution of butyl alcohol in CCl_4 .

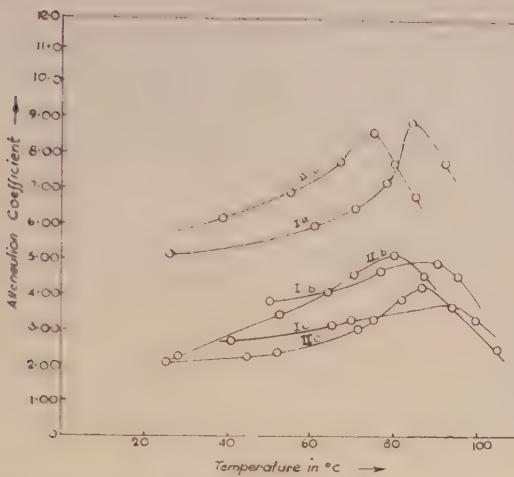


Fig. 3. Temperature dependence of the attenuation coefficient of the solution of iso-alcohols in CCl_4 .

Ia—30% solution of isopropyl alcohol in CCl_4 .

Ib—50% " " " " " "

IIa—30% solutions of isobutyl alcohol in CCl_4 .

IIb—50% " " " " " "

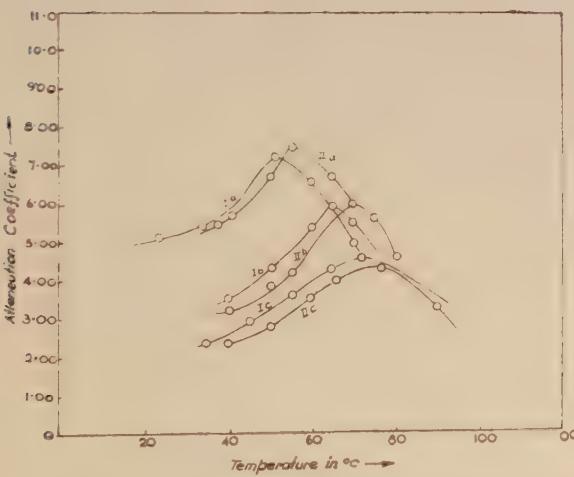


Fig. 4a. Temperature dependence of the attenuation coefficient of the solutions of lower alcohols in heptane.

Ia—30% solutions of *n*-propyl alcohol in heptane.

Ib—50% " " " " " "

Ic—70% " " " " " "

IIa—30% solutions of *n*-butyl alcohol in heptane.

IIb—50% " " " " " "

IIc—70% " " " " " "

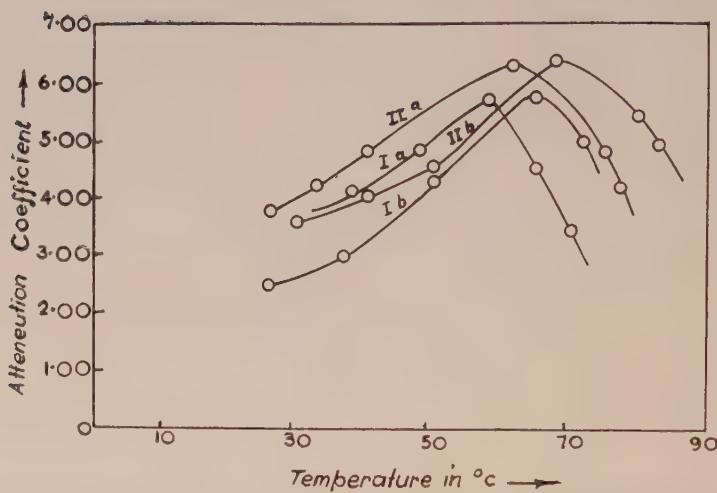


Fig. 4b. Temperature dependence of the attenuation coefficient of the solutions of higher alcohols in heptane.

Ia—30% solutions of octyl alcohol in heptane.

Ib—50% " " " " " " "

Ic—70% " " " " " " " "

IIa—30% solutions of heptyl alcohol in heptane.

IIb—50% 11 12 13 12 11 11

He-70% N H N H N H

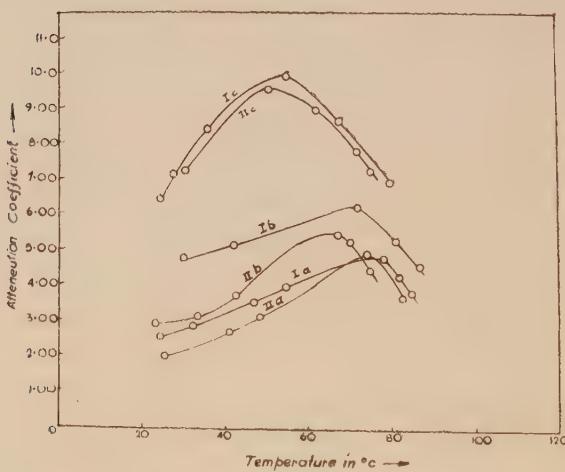


Fig. 5. Temperature dependence of the attenuation coefficient of the solutions of iso-alcohol in heptane.

Ia—70% solution of isobutyl alcohol in heptane.

Jb—50% 11 11 11 11 11

[18-70% solution of isopropanol ethanol] 1.0

IIa—70% solution of isopropyl alcohol in heptane.
IIb—50% " " " "

shows the maximum at 105°C while heptyl alcohol shows it at 100°C. The absence of any absorption maxima in the case of lower alcohols cannot be explained on the assumption that these occur at higher temperatures i.e. at temperatures higher than 100°C, because heptyl and octyl alcohols which have higher viscosity show their respective maxima near about 100°C. When the lower alcohols are dissolved in the solvents, carbon tetrachloride and heptane we get absorption maxima at certain temperatures as shown in Figs. 2, 3, 4 and 5. This difference in the behaviour of the pure liquids and solutions may be explained on the assumption that in the pure liquid most of the molecules are in the form of dimers formed by weak linkage through the H-O—H-O bond and as the dimers break up with the rise of temperature contribution to absorption from new single molecules increases gradually without attaining a constant value. In the case of the higher alcohols, however, the molecules being long, some of the molecules do not form dimers and exist as single molecules. As the viscosity attains the proper value with the rise of temperature of the liquid a maximum absorption is exhibited by these molecules in these cases.

An attempt was made to calculate the radius of the rotor from Debye's theory in the cases in which maximum absorption has been observed. The data required for this purpose as well as the values of τ , the time of relaxation and a , the radius of the rotor are given in Table I. It is interesting to note that the values of a , the radius of the rotor, is almost the same in all these cases, the mean value being about 1.96 Å. Evidently, the rotor is not the whole molecule in any of the liquids and the solutions and the common group present in the molecules being the OH group, the rotor may be identified with this group. In previous investigations the radius of the rotor for the OH group in aromatic compounds was calculated and it was found to be of the order of 1.5 Å (Ghosh, 1955a, 1954), but no such data for aliphatic alcohols are available. It cannot be expected that radius of the OH group as the rotor in the case of aliphatic compounds should be the same as that for the aromatic compounds, as the radius of such rotor is expected to be dependent on the bond angle and other factors. Ghosh (1955a) observed in *o*-methoxy phenol, a typical aromatic compound, the radius of the OH rotor to be 1.7 Å which is slightly larger than the value observed in the case of *p*-chlorophenol, *p*-chlorocresol etc., So, the rotor in the present case can be identified with OH group of the alcohol molecules.

The comparison of the curves for the pure liquids with those for their solutions thus leads to the conclusion that in the lower alcohols in the pure state most of the molecules are in the state of loosely coupled dimers and in the solutions these dimers break up into single molecules. Application of Debye's method in these cases gives consistent results and also furnishes much information about the state of association of the molecules in the liquids.

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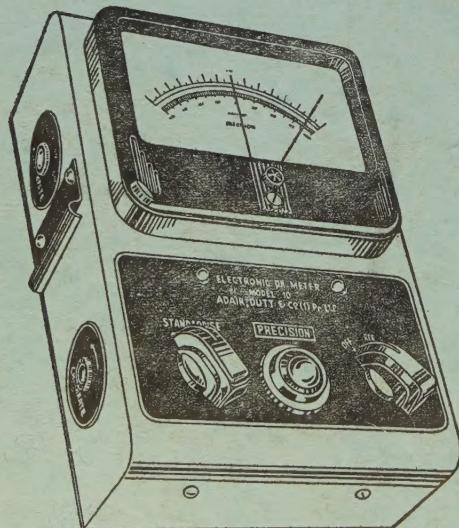
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